



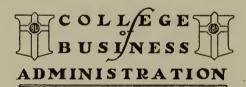




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# College of Business Administration

#### THESIS

Industrial Uses of the Milk By-Product, Casein

by

Herbert George Spindler (B. A. in Economics, University of Wisconsin, 1938)

Submitted in partial fulfillment of the requirements for the degree of

Master of Business Administration





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#### INTRODUCTION

What to do with his surplus milk has been an ever increasing problem for the farmer. Milk production varies with the seasons, weather and pasture conditions, the relationship between milk and some other agricultural commodity which the farmer might be tempted to produce in lieu of milk, and the ratio of feed grain prices to the farm price of butterfat. Consumption, on the other hand, is relatively constant throughout the year.

Since milk is highly perishable, it is necessary to dispose of it almost daily. This perishability, the shipping costs, public demand for cream and ice cream, particularly in the summer months, and for butter during the entire year, together with the surplus production of milk during the flush summer months, all make it necessary to separate huge quantities of milk before it is shipped. As approximately 90% of the separated milk is skim, there is created a problem of adequate profitable outlets for this product of high intrinsic value, containing, contrary to popular conception, almost all of the milk value with the exception of the fat element. Nevertheless, in the past the farmer has received little or nothing for this product. In fact, quantities of it have been unprofitably disposed of, or even dumped.

Casein production has been a partial answer to this involved problem. Domestic production in the twenty



years from 1916 to 1936 has almost increased eight-fold, from eight million pounds to forty-six million pounds.

Foreign production has declined relatively for the same period, imports in 1916 being ten million pounds and in 1936 sixteen million pounds. Per capita consumption was .21 pounds in 1916 and .49 pounds in 1936, more than a two-fold increase.

Casein has a number of significant features; it is a milk product used in the manufacture of articles rather than as a food; it is used in widely diverse forms ranging from paints to fibres, and from glue to plastics and medicines. With today's demand for unique products and the urgent call for substitute products, casein is vital. Much of the recent development of casein uses has been the result of planned chemurgic research.

Literature on casein is mostly confined to information on technical aspects of the topic. In the succeeding pages an attempt has been made to outline the business and economic aspects of the casein industry. This is the sequence followed: background of the industry, manufacture of the product, growth of the industry, discussion of each of the major uses, and, finally, the industry's social and economic implications.

#### I. BACKGROUND OF THE CASEIN INDUSTRY

## A. Nature of Casein

Casein may best be described by comparing it with the more familiar cottage cheese. Cottage cheese, in fact, is derived from the same source, skim milk, as is casein; the manufacture of both results in a residual product, whey, containing milk solids in substantial quantities. In the process of manufacture, both products form curds, and manufactured cottage cheese contains the same protein product which could have been used for casein.

simple. The curd is precipitated by addition of dilute acid, the enzyme rennet, or the natural souring or lactic acid method. The spongy cheese-like mass is then washed to free it of impurities, and is dehydrated by pressing and drying, and is ground into uniform powder.

Casein which is used for commercial purposes is a protein constituent of cow's milk. It is an elemental part of skim milk, which is the remainder after cream has been separated from whole milk by centrifugal force. Normally, 10% of separated milk is cream and 90% is skim milk. A general average of the principal constituents of cow's milk is as follows:

Water	87%
Casein	
Butter Fat	4
Lactose	
Minerals	
	100%

The percentages shown in the data above are only general averages and are subject to variances in specific cases. Since casein constitutes only 3% of skim milk, it can be obtained economically and in marketable quantity only where there are substantial quantities of this byproduct discarded by the dairy industry.

It is to a great extent the heavy demand for cream to be used as table cream, in ice cream, and in butter that makes skim milk available in sufficient quantity for use in the manufacture of casein. It is interesting to note that market quotations on milk and cream are based on their butter fat content, while little or no value is added for skim milk. Yet skim milk, and also buttermilk, contain almost the same content of solids as whole milk with the exception of the fat element. As a body-building food, skim milk is as valuable for human consumption as for young animals on farms, particularly calves, pigs, and chickens.

Whole milk is too expensive to be used in manufactured products such as glues, paints, fibres, plastics,

or paper coatings. Moreover, it is unsuitable because of the butter fat contained therein. Market whole milk, and the dehydrated manufactured milk products such as whole milk cheese, condensed milk, and evaporated milk leave no residue of skim milk. Skim milk is obtainable only where cream is in demand for some specific purpose, leaving the separated skim milk as a potential reservoir for the casein industry.

## B. Historical Background

The known use of casein dates back into ancient history. For example, its use as a binder for paint was referred to in ancient Hebrew texts which "urged the housewife to store curd and the husband to go forth into the hills to bring back the color earths for the autumn visit of the decorator when the house was to be painted for the Succoth."

Also in the eleventh century it was known that curd gives a viscous and very water-resistant adhesive when mixed with slaked or unslaked lime.

For years chemists have realized that great potentialities exist in the protein product of casein, and much research has been carried on in an attempt to widen the

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 315, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Hadert, Hans, "Casein and Its Uses", Chemical Publishing Co. of New York, N. Y., 1938

industrial uses of this product. Conspicuous progress has been made since 1929 both in the production and the utilization of it. Previous to that time, more than one half of the casein consumed in the United States was imported, but since then, even in spite of depression, domestic production has remained greater than it ever was before 1929, (1) and there seems to be a wealth of possibility still open for future developments.

## C. Relation to Milk Production

Expansion of casein production has taken place in areas where there has been increased demand for butter, cream, and ice cream, thus solving the problem of profitable utilization of skim milk. In the interest of cutting transportation costs, both cream and skim products are manufactured near the source of their production. As only 3% of the raw material results in casein, obviously transportation costs may constitute a large portion of the total cost of casein.

As contrasted with perishable, bulky milk (and skim), separated cream constitutes a relatively high value, low bulk item which can be economically stored in refrigeration for indefinite periods of time, and can be shipped long distances at only a small percentage increase in the total cost of the

<sup>1.</sup> United States Tariff Commission, "Trade Agreement Between the United States and Argentina", p. 6, Washington, 1942



product. It is these cream separating plants located near the source of production that are confronted with the disposition of skim aggregating 90% by volume of the original raw material.

The development of rural highway systems and the invention of auto trucks made possible larger plants handling larger volumes of milk, permitting in turn greater outlays in more specialized processing machinery.

On farms the general trend has been a decrease in the self-sufficiency element and the elimination of the farmer-to-consumer method (1) of marketing fluid milk, and in its place have appeared the milk dealers (2) who receive milk from large numbers of producers and distribute milk and bottling quality cream to roughly 60% of the population of the United States. Dealers are confronted with the problem of supplying a relatively stable fluid market and disposing of the "surplus" as best they can. As the milk must be disposed of, it is usually separated and the cream either is used for butter manufacture or is shipped to large metropolitan markets where it may be used in ice cream, for bottling cream, or it may be stored. Large dealers have an ad-

<sup>1.</sup> Some Boston milk dealers still tell of consumers obtaining their milk by dipper method direct from a jug to the consumer's odd container.

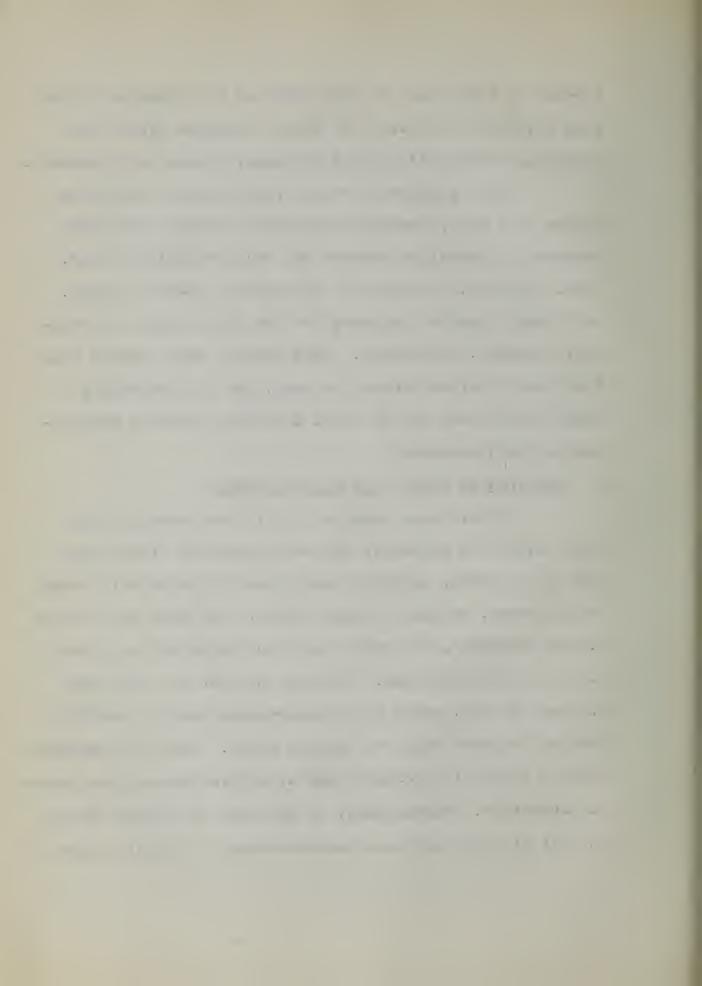
<sup>2.</sup> According to statistics assembled by the Federal Milk Market Administrator, S. W. Tator, Boston, Massachusetts, about 200 dealers receive milk from 15,000 farms and supply an estimated 1,000,000 consumers in the Greater Boston Marketing Area.

vantage in being able to ship milk and its products in carload lots and often can use certain equipped plants for handling "surpluses" of milk and manufactured skim products.

Milk production varies considerably during the course of a year, whereas consumption remains relatively constant. Production reaches the "flush" period in May, June, and July, and drops in the hotter, poorer pasture, late summer months, reaching its low point along in November, December, or January. Thus dealers must contend with the "flush" period production peak, and if they supply a fluid market they may be faced with only periodic manufacture of milk products.

# D. Relation to Other Skim Milk Products

Casein must compete for its raw material with other skim milk products, the most important items being skim milk powder, condensed and evaporated skim milk, skim milk cheeses, notably cottage cheese, and Greek and Italian brands of cheese, the market price of which may vary from \$.20 to \$1.00 per pound. Whatever the use to which skim milk may be put, costs of transportation usually prohibit hauling for more than one hundred miles. Thus, the manufacture of skim milk products must be carried on near the source of production. Furthermore, in the case of cottage cheese, and all the high moisture content Greek and Italian types of



cheese, their perishable nature combined with their relatively larger bulk makes it imperative that these products be
marketed within a radius of a few hundred miles. Contrarily,
casein and skim powder yielding approximately 3% and 8.5%
respectively, (as contrasted with approximately 15% curd
yield for cheese), are a more concentrated article and when
properly manufactured and dried are highly stable and can
be shipped any distance and stored for a considerable length
of time.

Marketing of the "soft cheeses" is limited to particular conditions. It is dependent upon the existence of surplus milk beyond fluid requirements located near a metropolitan market which can and does accept the type of cheese marketed at prices which are profitable to the manufacturer.

Skim milk powder is a concentrated food containing all the solids of milk with the exception of the butter fat. It is extensively used by bakeries and can be packaged easily, is comparatively light, and will keep indefinitely if it remains dry.

Condensed and evaporated milks are produced by vaporizing and eliminating approximately two-thirds of the water content, resulting in a high solid content product, rich in food values. Both condensed and evaporated milk are often used in ice cream manufacture.

Dealers separate milk to obtain the cream, and then look for the most profitable outlet available for skim milk. In the case of powder, evaporated and condensed, all the solids are utilized and form a portion of the finished product. In the case of skim cheeses more of the solids are utilized, but in the case of casein, of the approximate 9% solids remaining after the butter fat has been removed, only 3% of protein solids are derived, leaving another 6% not utilized, contained in the whey. Uses have been discovered for the utilization of the whey from casein, but at present the volume is still small. This aspect is discussed on page 91 under "Casein in Foods".

The reader may get the impression that, since a theoretical 50,000,000,000 pounds of skim milk are still not utilized except perhaps for stock feed on farms, the aforementioned skim milk products merely supplement and do not compete with casein. Although there is an element of truth in this conception, nevertheless, in practice it is found that concerns with large quantities of skim milk consistently use all this product, and they usually can dispose of it in various ways depending on the market prices at the moment. The 50,000,000,000 available pounds of skim milk will be used for other than animal feed if and when there is a sufficient accumulated demand for manufactured skim

milk products at a price to pay all the costs of manufacturing. These include machinery, overhead, plant facilities, transportation of raw material, and a price to the farmer which will induce him to relinquish the skim milk. If the volume handled is too small, manufacturing, transportation, and raw material costs may soon exceed the value of the product.



# II. THE MANUFACTURE OF CASEIN

# A. Manufacturing Procedure

The first operation performed in the manufacture of casein is precipitation which is caused by the action of a variety of acids, the predominating ones in this country being muriatic and sulfuric acids. "Small amounts of lactic acid casein are prepared. In other parts of the world such as the Argentine, New Zealand, Australia and formerly France, much lactic acid casein was prepared, and in this case the lactic acid is frequently formed by allowing the milk to self-sour. Sugar, which is one of the constituents of skim milk, may ferment to yield lactic acid which, in turn, precipitates the casein."

(1) Hydrochloric acid may also be used and some casein is precipitated by the action of rennet.

The choice of the reagent is usually determined by the needs of the manufacturer's customers, for different industries prefer different types of casein. For example, the plastics industry usually desires rennet casein, a type not preferred, as a rule, by the paint, paper, and glue industries. The hydrochloric acid type is desirable if milk sugar is to be recovered from the whey left after precipitating the casein, for sulfuric acid will leave calcium

<sup>1.</sup> Atwood, F. C., "Aralac", p. 2, American Dyestuff Reporter, March 30, 1942

sulfate in the whey.

Since only when the curd is precipitated properly can it be washed free from excess acid and constituents of the whey, it is most essential that there be a precise control of the precipitation. The most important factor in this process is the intensity of acidity at which the separation of curd from whey takes place. "Either insufficient acid or an excess of acid is detrimental to the production of curd that will make a finished casein of the highest quality."

After proper precipitation, the whey is drained off as quickly as possible, for it is more difficult to wash the curd, the next step in the process, if it is left too long in contact with the whey and a casein of low solubility results. The washing must be thorough if casein of good color is desired.

Next the curd must be de-watered so that the proportion of water shall not exceed 55% to 65% before drying. This process facilitates drying and reduces contamination. In some cases, draining for a few hours may be sufficient, but frequently either hand or power presses are required.

As soon as the curd is properly de-watered, it

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 125, Reinhold Publishing Corp., New York, N. Y., 1938



should be ground and prepared for the next step in the process which is drying. Decomposition may set in if it is allowed to stand too long, and once the drying process is started, it should be completed without interruption or the curd may mold and deteriorate. A shaker screen may be used with good results for this process, or a curd mill which has provision for spreading the curd on trays as it comes through the mill may be employed. "Control of the temperature and humidity of the air is important in any type of drier. Recirculation of a portion of the heated air through the drier, especially during initial drying, prevents case hardening of the curd particles, facilitates the balance of the drying process, and effects a saving in the heat units which are required." (1) If the casein has been properly dried it will be fine and granular, but if it was dried at too high a temperature, particularly at the beginning, it will be in sheets and much harder to grind.

The dried casein may be ground to give it a more uniform grain and appearance, as well as a lighter color, or it may be sold to dealers in its unground form. Some manufacturers prefer to grind it themselves to suit their particular requirement. The finished casein is packed in

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 128, Reinhold Publishing Corp., New York, N. Y., 1938

burlap bags with liners of strong paper or closely woven cloth. If it is to be stored for any length of time, a dry clean place having as little change in temperature as possible should be selected.

## B. Essential Equipment

Some of the essential equipment required for the manufacture of casein would include storage vats for skim milk and whey, precipitating vats, curd presses, drain vats or racks, curd grinder, and a drier. If cooked curd should be shipped wet to a central drying plant, the precipitating vat only would be needed.

The most commonly used type of vat is made of wood because it is less expensive and withstands acids.

Iron vats are sometimes used, but they have the disadvantage of being subject to corrosion.

A continuous type of curd press has displaced for the most part the old manually operated type of press, for it allows the precipitated curd to be placed in the drier more quickly than does the old press. From 500 to 1000 pounds of dry casein per hour is the capacity of these continuous presses.

The drain vat or rack is used in methods that produce a curd capable of draining well enough for grinding without pressing. "The drain vat is built much like a precipitating vat except that it has a false bottom of perfo-

rated sheet iron through which the whey and wash water drain, leaving the curd behind."

(1) Redwood, heartwood, or cypress is most suitable for the drain rack, for lightness and ability to stand moisture are essential. 5000 pounds of skim milk can be handled by two such drain racks.

Since favorable drying conditions are dependent upon the correct grinding of the curd, it is important to have a curd mill with both a shredding and a beating action.

There are two types of driers, the tunnel drier and the continuous drier, and while the tunnel type is less expensive to buy, the continuous one proves more economical in operation and results in a superior product.

## C. Early Manufacture

The early manufacture of casein was on a small scale and by methods chosen "for simplicity, convenience, and low capital investment in equipment rather than for production of casein of uniformly high quality. Many manufacturing procedures were in use, most of them of long standing and ill adapted to precise control." (1) Thus a great variation resulted in the quality and properties of the casein. For this reason many of the industries using it preferred imported casein which seemed to be more uniform.

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 118, Reinhold Publishing Corp., New York, N. Y., 1938



### D. Improved Procedures

A great improvement was noted in the manufacture after the Bureau of Dairying of the United States Department of Agriculture and state agricultural experiment stations developed improved manufacturing procedures. Not only was improvement noted in the casein manufactured by small producers, but there was also an increase "in production of casein by large plants having new and more expensive equipment, closer technical supervision, and more definite commitment to supply a product of uniform properties and good quality to meet their customers' requirements."

(1) A reduction in the cost of manufacture resulted also.

Some of the principal changes in manufacturing methods were:

- "1. More general use of methods giving a granular curd from which impurities are easily washed, thus yielding casein containing less acid and ash.
- 2. Development of continuous methods of precipitation.
- 3. Elimination of the old hand process of pressing the wet curd by producing curd that drains well enough to be ground without pressing.
- 4. Quicker drying by securing a curd that withstands higher temperatures in the tunnel drier, or by using a continuous drier." (2)

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 113, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Ibid. p. 114

# III. GROWTH OF THE CASEIN INDUSTRY

## A. Slowness of Growth

Not until 1900 did casein production and consumption in the United States begin to become important. As early as 1780 C. W. Scheele had recognized casein as a constituent of milk, together with butter fat, lactose, a little extractive substance, salt, and water. (1) Casein, however, had to await a demand from industries in which it is accepted today. Glazed paper and veneer woods are comparatively new commercial developments owing part of their success to casein's qualities.

In considering the slowness of growth of the casein industry many factors must be kept in mind. Wisconsin, today's foremost producer, did not become a State until 1848; California, the second highest producer, was just receiving a deluge, not of farmers, but of gold prospectors in 1848; railroad building, begun in 1820, did not reach its climax until 1850; the automobile was not available except to a limited public in 1910; and surfaced roads were still a rarity. Shipment of milk from Vermont to Boston had not begun until 1900, and refrigerator tank cars were a comparatively recent development. It took a World War to

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 11, Reinhold Publishing Corp., New York, N. Y., 1938

hasten industrialization which led of necessity to specialization, and also to the farmer's "overproduction", with its resultant effort to expand the markets for farm products.

No doubt the price of casein has been a limiting factor in the production of domestic casein. It appears that established foreign producers could deliver casein in the United States at a price, ranging from 5g to 15g per pound, below the cost of domestic production. A study by the United States tariff commission attempted to determine the cost of production in the chief competing nation, Argentina, and although the commission reported that no comparable conclusion could be drawn from the evidence available, yet a  $2\frac{1}{2}g$  tariff per pound was imposed in 1922, and raised to  $5\frac{1}{2}g$  in 1930. (1)

Even more important than the element of foreign competition on the basis of costs is the fact that Argentina and France put out a product more consistently standard.

Only within recent years have casein producers become conscious of the necessity of using rigid controls in every step of the manufacturing process. Previously, so much of the casein was of such irregular standards that manufacturing consumers of it were uncertain of their products because

<sup>1.</sup> United States Tariff Commission, "Trade Agreement Between the United States and Argentina", p. 3, Washington, 1942

of its undependability.

There were good reasons for this, as skim milk was at one time considered a waste-product of the milk industry. Many farmers separated their milk on the farm, delivering the butter fat in the condensed form of cream, and using the skim to feed his young stock. "It is not sound economics thus to convert ten pounds of milk solids into one pound of edible meat solids, but, without a more profitable means of disposal, it is the most practical way of utilization."

Dr. F. C. Atwood summarizes the situation on the available supply of skim milk as follows:

"To induce the farmer to bring more of his whole milk to market, he must receive more money to cover at least three items; first, the extra expense of hauling the bulkier whole milk; second, enough to compensate him for the substitute feed he would need for his livestock; and third, compensation for changing his method of operation." (2)

Another factor contributing to the lag in domestic production of casein was the fact that much of it was produced haphazardly as a side-line, or a flush-period extra, and second, it was considered unimportant to take pains in controlling its production. Improperly dried casein became rancid and odoriferous. The fact that substantial quantities of butter fat had not been eliminated made

<sup>1.</sup> Excerpt from a letter addressed to the writer from Earl

O. Whittier, Senior Chemist, U. S. Dept. of Agriculture 2. Rayon, p. 36, November 1936

casein much more liable to spoil and was always a detriment in manufacturing casein articles. Machinery was poor and inadequate; its installation was, and still is expensive, and skill is required to process a high-grade product. "Casein cannot yet be made in every milk product manufacturing plant."

In any case, casein production is limited to the available supply of milk. Since fluid milk brings the largest return, fluid requirements are met first; but to-day's available supply of skim milk which is dumped or used to feed farm animals exceeds 50,000,000,000 pounds, from which 1,500,000,000 pounds of casein (2) could theoretically be obtained. However, "casein factories are not accessible to many dairy farms and it is uneconomical to transport bulky skim milk long distances for casein manufacturing." (3)

## B. Favorable Developments

Although there were hindering factors and limitations, there were also developments favorable to the growth of the milk industry and its by-products.

So long as urban centers were small, the small scale "from-producer-to-consumer" relationship could exist. However, coincident with the growth of large cities, prob-

<sup>1.</sup> Rayon, p. 36, November 1941

<sup>2.</sup> Dr. F. C. Atwood, Seventh Annual National Farm Chemurgic Conference, Chicago, Illinois, March 26, 1941

<sup>3.</sup> Rayon, p. 36, November 1941

lems developed in milk distribution. Dealers were forced to obtain milk from farms farther distant from the city being In the Greater Boston Marketing Area, for example, supplied. 60% of the milk is produced on Vermont farms. Milk from a greater number of farms was delivered to larger volumed country stations, preparatory to milk and cream shipments to metropolitan areas. Improvements in roads and refrigeration thus became important factors. Also, large handlers were able to devote a certain few of their country plants to manufacturing purposes, thereby obtaining a maximum use of necessary manufacturing equipment. Pasteurization, whatever its health benefits, has necessitated considerably greater cost due to the additional need of pasteurizing vats, agitators, coolers, boiler heat and more refrigeration facilities. This, too, has tended to encourage large scale operation at plants concentrated on transportation lanes.

Larger scale industry, in turn, resulted in efforts to improve technical aspects of manufacturing casein, together with the most economical way of handling it. Separation today is done at nearly 100° F. with vacuum-centrifugal separators. Thus the skim is already preheated (saving heat) and the improved separators are economical as they eliminate what previously amounted to substantial butter fat losses. Incidentally, this has resulted in a better skim product for casein as butter fat is detrimental in casein manufacture.

Vast improvements, too, have been made in the important phase of drying casein. The use of driers with controlled temperatures and controlled humidity with a pre-ground casein result in a much more uniform product, consistent from day to day. It is not difficult to manufacture casein, but to manufacture a consistently uniform product necessitates diligent control of every step in the manufacturing process beginning with the skim milk's condition and substance. For although the variations of milk solids have their limitations, no product from a single cow is ever constant.

No doubt the most important reason for the growth of the casein industry is the expansion of uses to which casein may be put. Theoretically sufficient skim milk is available in the United States to produce an additional 1,500,000,000 pounds a year. To date however, the limiting factor has been the market demand for casein at a profitable price to the manufacturer. Not only has its use in paper coating and glues been expanded, but its use has been extended to paints on a commercial scale, to plastics in a more or less developmental stage, and within the last few years to cloth and felt production on a commercial scale.

#### C. Production

Commercial production of casein began in the United States about 1900. By 1923, production aggregated 14,500,000 pounds; by 1929 this figure was doubled; by 1936

it had trebled; and since that date, despite war dislocations, production has continued upwards. This upward trend in domestic production is shown in Table I, page 30.

In 1930, when consumption soared to 60,000,000 pounds, 316 plants produced casein; in 1932, the number of plants had declined to 195 as a result of a precipitous drop of price, but it rose steadily to 552 in 1936, and to 624 in 1937. The variation in output is reflected mainly by the number of plants producing, whereas the average output per plant has shown little deviation. Of the total domestic production approximately 80% is manufactured in Wisconsin. California. New York. and Illinois. All plants in California and a few of those in Wisconsin. New York, and Vermont are large; but small plants produce the bulk of the output for the country as a whole. Approximately one quarter of the domestic production occurs in the flush months of May and June. Fortunately, because seasons in Argentina are the reverse of those in the United States, our heaviest imports of casein from that source occur in the last six months of the year.

## D. Imports

In considering the trend of imports, tariff duties should be kept in mind, as the first duty on casein in 1922

<sup>1.</sup> United States Tariff Commission, "Trade Agreement Between the United States and Argentina", Washington, 1942
2. Ibid.

gave domestic producers a price advantage of  $2\frac{1}{2}g$  and a second addition in 1930 gave them  $5\frac{1}{2}g$  per pound margin. Recently, however, a trade agreement with Argentina signed in October 1941, reduced the rate to  $2\frac{3}{4}g$  per pound. Foreign countries must compete with our domestic production at foreign cost of production, plus shipping costs, plus a flat rate of duty per pound. As a result of this competition, import quantities vary considerably with the price of the domestic casein quotations.

Thus although domestic production and consumption have shown a relatively constant increase, imports remained constant from 1923 to 1930, and then dropped sharply for two important reasons: one, the drop in price from  $15\frac{1}{2}g$  per pound in 1929 to 7.5 g per pound in 1931 as a direct result of the depression, and two, the increase from  $2\frac{1}{2}g$  to  $5\frac{1}{2}g$  per pound on casein imports. Table I on page 30 shows that  $5\frac{1}{2}g$  was equivalent to more than 1/3 of the domestic price quotation in every year from 1930 to 1941. Only with the increase in the price of casein have imports again increased in 1939.

Import figures for 1942 are not publishable; however, with the decrease of duty from  $5\frac{1}{2}$ % to  $2\frac{3}{4}$ % per pound it seems reasonable to forecast that imports today are substantially on the increase.

Casein: United States Production, Imports for Consumption, and Prices 1923-41 Table I.

																						1
	Price Quotations of Domestic Casein (1)	Cents per Pound	3	12.8	3	•	5	9	-		•	•	•	13.5	15.5	•	17.0	•	•	(2)	(2)	
	Unit Value of Imports	Cents per Pound		5.1	•	•		8.4	8.1	9.6	•	•	•	•	12.1	•	•	0	<b>σ•</b> α	•	16.6	
	Apparent Consumption (Production & Imports)			73.5			72.7	•	•	•	32.4	•	38.4		57.9	•	ŝ	•	5.	38.0	39.9	
	Imports	Pounds	6	24.5	5	•	•	•	•	•		•	•	•	27.4	•	•	•	•		•	
	Domestic Production	Millions of		•	•	•	•	•	•	•	•	•	•	•	30.5	•	•	•	•	•	•	
	Year		O	တ	တ	O	O	O	O	O	S	တ	O	တ	1929	O	တ	OB	တ	(C)	O	

20-30 mesh, in 5-ton lots, f. o. b. plant Not available

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Last quarter estimated at first 9 months' rate

Source: United States Tariff Commission, "Trade Agreement Between the United States and Argentina," Washington, 1942

### E. Consumption

consumption of domestic casein has been increasing steadily, having risen from 40,000,000 pounds in 1923 to 74,000,000 pounds in 1940, almost doubling in 17 years. In considering the steady increase in consumption, one must give thought to the industrial uses to which casein is put. Its use in paper coating, especially in high-grade advertising types, increased due to expansion of advertising. Normally, about 75% of our consumption is used in coating paper, and the decrease in output of this type of paper, which at present has lessened casein consumption, appears to be but a temporary phase.

Large quantities of casein are also used in paints. Casein consumption, therefore, is affected by increases or decreases in paint output. The use of casein herein, as in other products, is marked by peculiar characteristics which make its content more valuable for some uses and less favorable for others. Contrary to popular public opinion, "substitutes" when planned for specifically prescribed needs are often superior to the original product. This seems to be true of the use of casein in paints, for casein paints have superior qualities for certain prescribed uses. Although the market has slumped at present, for civilian use, casein paints seem to be adapted and find an outlet today for use as camouflage coverings.

Casein used in glue received a large commercial boost as a result of the World War demand for a strong water-resistant glue for use in airplanes. As a direct result of the combined research efforts of the Forest Products Laboratory, and the University of Wisconsin, both at Madison, Wisconsin, casein glue has been used extensively in veneers and plywood products. Incidentally, at present, casein glues are enjoying a boom again in airplane propellers.

Although plastics are more commonly used in foreign countries than here, nevertheless, progress is being
made in casein plastics output due to the fact that they
have been put to use in airplane construction. For the
most part, slow processing operations in the making of casein plastics have prohibited their use in many fields because of higher costs.

In fibres, casein has reached commercial importance in the last two years. This is an entirely new outlet for casein with possibilities which appear almost limitless at present. Research has long recognized great possibilities in this complicated protein product because of its close similarity in chemical makeup to wool. See Table II, page 33.

Table II. Similarity of Casein Fibre to Wool Percentages of Total

ELEMENT	CASEIN FIBRE	NATURAL WOOL
Carbon	7.5 23.0 15.0	49.31 7.57 23.66 15.86 3.6 .0

Source: Textile Recorder, "The Manufacture and Property of Casein Fibre", June 6, 1939

Dr. Ferretti, an Italian chemist, began work in 1924 on a brittle, unpliable German product and by 1935 the improved product was being used as a substitute for wool. In the United States where there is no wool shortage, every effort is being made to develop a distinctive fibre with merits of its own.

Fortunately casein is versatile, adaptable to uses in many and diverse industries. Therefore, casein producers and casein outlets are not dependent upon any single industry.

### IV. CASEIN IN PAPER MAKING

### A. Earliest Use

It is believed that casein was first used commercially in this country in paper coating between 1890 and 1900. Previously, it is claimed, green curd was used with good success as far as color, odor, and adhesive strength were concerned; but it was impossible to prevent the curd from spoiling, especially in hot weather.

### B. Extent and Type of Use

Until recently about 75% of the total amount of casein was used in the paper industry, mainly in the preparation of coated or enameled papers, which are used for lithographic work, for magazines and other printing, and especially for high-class advertising where the perfection required of the illustrations necessitates the use of half-tone plates with a large number of lines per inch. To prepare such papers mineral matters are mixed with a solution of an adhesive and this mixture is applied in a thin, even layer to the surface of an ordinary sheet of paper. It is the function of the adhesive to bind the mineral matter, which forms a surface receptive to ink, firmly enough to the paper to prevent its being removed or "picked" off during the printing operation. (1)

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 293, Reinhold Publishing Corp., New York, N. Y., 1938

Three adhesives, starch, glue, or casein, may be used in the coating of paper, but the amount of casein used far outweighs that of the other two combined. In fact, in "Germany, inadequacy of German production of casein for the needs of the paper industry appears to be a cause of concern in the effort to make the nation self-sufficient, both glue and starch being considered inferior to casein."

Mr. Hans Hadert reports in his book, "Casein and Its Uses", (1938)

(2) that Germany uses 3000 tons of casein annually in the paper industry.

Perhaps the greatest advantage of casein as an adhesive is the ease with which it is rendered waterproof. The coating may be made so resistant to water that the paper can be washed with a sponge without injury. Such a condition is impossible with starch, and though possible with glue, is attained only with great difficulty and expense.

Casein has also been used in smaller quantities in several paper converting specialties. For example, it has been used to some extent for various purposes in the wall paper industry. In papers known as "varnish tiles"

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 293, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Hadert, Hans, "Casein and Its Uses", Chemical Publishing Co. of New York, N. Y., 1938

it was used as a size coat to support the varnish, but its increasing cost made the substitution of a vegetable product advisable.

In the manufacture of playing cards, it has also been used. In conjunction with shellac dissolved with alkali, it serves as a top varnish for the cards.

While the Department of the Interior at Ottawa, Canada, claimed it could replace fish glue in making strong and durable waterproof and fireproof asbestos paper, boards, etc., its use for such a purpose does not seem to be very extensive, for Mr. Sutermeister points out that three of the largest makers of asbestos products do not use it in any of their work.

Once considerable quantities of casein were used in the production of the so-called "onion-skin" grade of writing paper, and although very good results were obtained, the cost of the casein was far too great, so its use was abandoned in favor of cheaper materials.

An increase in the use of domestic casein was noted after 1930 when the tariff on imported casein was increased from 2.5 to 5.5 cents a pound. (2) At this time casein manufacturers had the domestic market without much competition.

<sup>1.</sup> Sutermeister and Brown, "Casein and Its Industrial Applications", p. 311, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Paper Trade Journal, "Casein for Paper Coating", Vol.96 January 26, 1933

## C. Improvements in Manufacturing Techniques

Perhaps another reason for a marked increase in the use of domestic casein in paper is that now casein manufacturers are much more careful in the preparation of the product. It is better standardized and cared for, and also, of course, the paper coaters know more about handling it to better advantage. When it was first used, the dealers used to mix the casein with the alkali necessary to the solution before delivering it to the consumer, and great amounts of borax and soda were used, apparently because the alkalines were cheaper than the casein. The paper coater had no choice of his solvents, and also the high alkalinity of the dry casein seemed to cause deterioration if the material was stored for any length of time. Real progress in the use of casein began only after this condition was remedied by the product being delivered unmixed.

In 1933, O. E. Reed, Chief of the Bureau of the Dairy Industry, extended an invitation to manufacturers and users of paper coating casein to attend a conference at the United States Department of Agriculture to consider suggestions for establishing a scheme of grading casein according to its paper coating quality. Dairy scientists co-operated with the Bureau of Standards and the results of three years of research were discussed. Mr. E. O. Whittier of the Dairy Research Laboratories stressed the fact

that variation in the procedure of manufacturing affected the properties of the finished casein. For example, the degree of fineness is very important. If the casein is too coarse, an undesirably long soaking is required to permit the water to penetrate the coarsest pieces; while if it is too fine, it is likely to lump when mixed with water, and unless it is completely soluble, the undissolved particles are likely to work up into the brushes of the coating machine where they will collect until the brushes can no longer hold them when they will drop off onto the paper and form lumps in the coating which are ruinous to the printing plates.

may cause putrefaction to begin, and the creation of an objectionable odor will result. Discoloration may be caused by allowing the casein to dry at too high a temperature for too long a time; or if the drying of casein is too long delayed, the moist curd will likely mold and cause white flakes which may be insoluble. Green spots or "eyes" may result from an excessive percentage of fat in the casein.

Mr. S. P. Gould, also of the Dairies Laboratories,

<sup>1.</sup> Paper Trade Journal, "Casein for Paper Coating", Vol. 96, January 26, 1933

found that foaming tendencies, which cause trouble for the paper coater, might be caused by too rapid agitation during the precipitation of the curd, by the use of temperatures below 95° F. during precipitation, or perhaps by insufficient washing of the curd.

(1) Much frothiness is likely to cause innumerable small pits in the coated paper.

This foaming of casein dispersions has been such a troublesome and costly factor that the Research and Development Laboratories of the Casein Company of America tested many compounds and products to find the most effective antifoaming agents. There are two methods that may be used to overcome the foaming: "One, adding a defoamer to prevent it, and two, adding a defoamer to disperse or kill it once it has been formed. Obviously, it is best to overcome foam by preventing it--but even then it is well to be able to control foam if it should form in a certain mixture, perhaps through the additive action of another foamy material in the mixture. Also, although it may be desired to add the defoamer to the mixture when preparing it, generally much less defoamer is needed when it is sprayed or sprinkled onto the foamy solution since the defoamer is then present only when and where needed." The tests showed that the best

<sup>1.</sup> Paper Trade Journal, "Casein for Paper Coating", Vol. 96, January 26, 1933

<sup>2.</sup> Casein Company of America, "Protovac", p. 45, Bainbridge, New York

 defoamer to use to prevent the foaming of casein was not the best one to dispel foam once formed.

# D. Recent Decline in Consumption

Today's war crisis has caused a sizable decline in the amount of casein used for paper making, for there has been a precipitous drop in the output of business catalogs, brochures, and such. The automobile industry, for example, used to issue them by the million. It was estimated that there would be "an estimated 75--80% crimp in the production of those casein-coated papers which accounted for 40,000,000 of the 60,000,000 pounds of casein used in 1941."

<sup>1.</sup> Business Week, "Casein at the Bat: Product of Many Uses", p. 101, Sept. 12, 1942

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#### V. CASEIN PAINTS

### A. Early History

As was pointed out in the historic background of casein on page 6, its use as a binder for paint is an exceedingly old art. "The interiors of many European Cathedrals of the 14th and the 15th centuries today have the same casein paint that was applied when they were constructed, and the colors remain bright and unfaded."

The system of the housewife preparing the "clabber from skim milk while the painter brings freshly burned lime and earth colors to mix the paint on the job" is still used in rural Hungary and in the villages of many parts of Middle Europe.

During the early history of the United States great quantities of whitewash were used both for interior and exterior painting. The curds from skim milk were frequently mixed with the slaked lime and water, and while whitewash still enjoys wide use, most of the formulas for it now call for substantial amounts of casein.

Since 1890, factory made casein paints in powder form, ready to be mixed with water for applications, have

<sup>1. &</sup>quot;Milk Fiber Cloth Now Being Made" p. 7 Wisconsin Agriculturist and Farmer, Nov. 29, 1941

<sup>2.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 315, Reinhold Publishing Corp., New York, N. Y., 1938

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been sold in the United States, but it was not until 1928, however, that casein paints equalled in amount flat wall paints of glue-bound calcimines.

### B. <u>Kind of Casein</u>

While preference seems to be given to the casein of domestic manufacture, some is imported from Argentina and Australia. A casein of fairly high viscosity is necessary to make a paint with satisfactory brushing qualities, so usually a sulfuric acid or hydrochloric acid casein is found to be more satisfactory than lactic acid or grain curd casein. (1)

### C. Types of Casein Paints

A marked increase in production of paints containing casein followed the development of greatly improved paints that could be sold in the form of pastes or powders, which made the mixing for use much quicker and easier. All the painter has to do is to dilute them with water and apply. The powder form is cheaper for it costs less to manufacture and less to distribute. In the paste form enough water is added to hold the casein in solution, but the painter must add more before applying.

There seems to be little difference in the merits

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 336, Reinhold Publishing Corp., New York, N. Y., 1938

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of the two forms, except commercially. Some dealers argue that powder paints have been so long associated in the public mind with calcimine that it is difficult to sell a superior product at the necessary higher price. However, paste paints have been controlled since their origin by a patent license structure, and "the paint industry seems to be traditionally opposed to patent control of paint products." (1) Most large manufacturers make both forms.

#### D. Uses of Casein Paints

The principal use of casein paints so far has been for interior painting, although recently it is finding increasing application in exterior painting, chiefly on cement, stucco, brick, or other surfaces on which a paint readily permeable to moisture is satisfactory. Considerable interest in exterior casein paints was stimulated by the extensive use of them at the Century of Progress Exhibition at Chicago in 1933 and 1934. Germany also has been using them in increasing amounts because of a shortage of vegetable oils. Anyhow, as Dr. F. C. Atwood pointed out in an address he made on "Modern Casein Paints" before the International Society of Master Painters and Decorators, one hundred gallons of interior paint are used for every one gallon of exterior. He estimates that 750,000,000 square feet of floor

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 329, Reinhold Publishing Corp., New York, N. Y., 1938

space of construction is the annual average, of which 55% is residential, 10% educational and institutional, 5% public buildings, 30% commercial and industrial. 65% to 75% of the paintable areas will call for decorative paint only.

Casein paints have also some application for special purposes. They are very suitable for plastic paints, and because of their highly porous nature, for acoustical paints. If Latex is added, the dried film becomes particularly elastic and stable against moisture; therefore such mixtures are used for street marking paints which must possess a great resistance to wear. (2)

Artists' water colors are often made with casein, and one advantage of its use here is that more water resistant paintings can be made than when water colors made with animal glue as a vehicle are used. Also casein colors do not need to be protected by a glazing coat, and thus they retain their flat surfaces and clarity of color. For this reason, architects widely use casein water colors.

Often in theatrical scenery, casein paints are used after additional fire-retardant chemicals have been added.

<sup>1.</sup> Atwood, F. C., "Modern Casein Paints", Plastics Products, Vol. 10, March 1934

<sup>2.</sup> Hadert, Hans, "Casein and Its Uses", Chemical Publishing Co. of New York, N. Y., 1938

Steel molders sometimes spray casein paints on the surfaces of molds to obtain castings with clean surfaces.

Then there are certain casein varnishes on the market which are used for several purposes. They may substitute for shellac to use as a coating for textile bobbins, and as coatings or dressings for paper, leather, or rubber.

Cardboard containers, when coated with casein varnish, may be made impermeable to oils.

Wooden containers for butter are often so varnished to prevent taint in the butter.

These varnishes also serve as sealers on wood treated with creosote to prevent the bleeding of the creosote into the paint applied over it, as primers for plaster walls over which architectural lacquers are to be applied, or for wooden furniture to be coated with lacquer.

Wall paper may be made washable by using a casein varnish as a final size. This is the largest use of casein varnish. One manufacturer is said to use ten tons monthly for this purpose. (1)

Casein is also used to some extent as an emulsifying agent in making aqueous emulsions of oils or metallic

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 345, Reinhold Publishing Corp., New York, N. Y., 1938



soaps for various industrial purposes. Mineral oil emulsions, for example, stabilized by casein may be used in textile dyeing and emulsions of a gasoline solution of aluminum stearate are now patented for waterproofing rock wool fibres. Unusually flexible coatings for paper, textiles, and leather are now made from aqueous emulsions of casein with rubber or rubber latex with added dyes or pigments.

Emulsion paints, however, while now quite widely used in Europe, both for interior and exterior work, seem to be commercially unimportant in the United States. They do not seem to meet the expectations of American property owners, and American-trained painters find them poorly adapted in working qualities for application here.

# E. Advantages of Casein Paints

Some of the advantages of casein paint over other paints are:

- 1. The cost is lower, for the thinner (water) is very inexpensive, and in casein paint the thinner does not become a part of the paint film in its permanent and final form.
  - 2. It is less expensive to apply, for fewer

<sup>1.</sup> Steel, "Water Thinned Casein Paint Shown To Have Many Desirable Features", p. 54, Vol. 100, January 25, 1937

 operations are needed; hence, a shorter time is required for completion of the job. Only one coat without sizing may be used, and it dries more rapidly and leaves no lingering odors.

- dead flat surface with high diffuse reflections; freedom from 'shiners'; clear, soft colors in pastel tints; and freedom from yellowing in subdued light."

  This high reflecting power means a saving in lighting bills to factory owners, owners of large warehouses, managers of large offices, etc. Operators of large public buildings are becoming more and more interested in this aspect of casein paint, for the cost of painting would be minor to the cost of extra lighting. If suitable pigments are used, these paints will provide high reflecting power for ultraviolet light, and so biologically are helpful.
- 4. The porosity to water vapor permits casein paints to be applied to plaster while it is still wet, and it does not interfere with the proper drying out of the plaster thereafter; and the fact that they "also have a high lime-resistance, a rare quality in paints, permits them to be used over cement or lime-mortar, even while

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 328, Reinhold Publishing Corp., New York, N. Y., 1938

 they are still wet." (1)

5. It is also singularly resistant to the accumulation and retention of dirt and grime, making it particularly suitable for use in cellars, warehouses, and factories. Soot, dust, etc., seem to collect less rapidly and wash off more easily.

### F. <u>Disadvantages</u> of <u>Casein Paints</u>

There are, however, some disadvantages in the use of casein paint.

- value as a protective coating for wood against weathering, stucco or concrete against absorption of water, or any metal against corrosion. Nonporous casein paints for architectural uses have so far made little progress commercially, because they are more expensive than oil paints and have too few advantages over them.
- 2. It stains more easily from grease or liquids and will not stand the hard scrubbing that oil paints will.
- 3. It is more subject to the growth of molds and decomposition of the vehicle when exposed to warm, moist atmospheres than oil paints.

<sup>1.</sup> Little, A. D., "Paint From Milk", p. 53, Scientific American, September 1934

# G. Extent of Use

In 1938 it was estimated that the production of casein paint in the United States was probably in excess of thirty-five million pounds, and since the Federal Specification requires a minimum of 10% casein in powder paints and 6.5% in paste paints, "the annual consumption of casein for manufacturing casein paints is probably at least 2.75 million pounds. With the addition of that used for calcimine and varnish products, the total consumption annually may be as much as 3.5 million pounds out of a total annual consumption of 60 to 70 million pounds of casein."

The principal merchandising impetus primarily comes from the makers of water paints, and now that these casein paints "are more than doing their share in camouflage, passive defense and black-out work,"

(2) there should be a still greater consumption.

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 347, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Atwood, F. C., "Dairy Chemurgy", Speech presented at the Eighth Annual Chemurgic Conference, Chicago, Illinois, March 25, 1942

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#### VI. CASEIN GLUES

#### A. Early History

Archaeologists report "that the craftsmen of ancient Egypt, Greece, Rome, and China used casein glue in their finest cabinet work, some of which is still to be seen in several museums. European woodworkers of the Middle Ages apparently understood the art of gluing with crude casein glues, an art that continued to flourish in a small way down to modern times."

### B. Manufacture in United States

The manufacture of casein glue as a separate industry, however, seems to have started in Switzerland and Germany in the early part of the nineteenth century, but it was practically unknown in the United States until 1917.

Previous to this date, casein glues and sizes were used for paper coating, but it was not until the United States' entrance into the World War, when there was a need for water-resistant glue for the construction of military aircraft, then chiefly made of wood, that a sudden interest in casein was aroused. Very soon, the manufacture of it became a thriving industry, and although aircraft construction later shifted largely to metal, the use of casein glue became firmly established in other woodworking

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 233, Reinhold Publishing Corp., New York, N. Y., 1938



industries in which water-resistance was advantageous.

United States by at least seventeen companies, operating twenty plants. In addition to these commercial producers, an indeterminate number of concerns make casein glues for their own use. During 1938 over seven million pounds were manufactured.

Table III. U. S. Production of Casein Glue

Year	Quantity in Pounds	<u>Value</u>	<u>Value</u> per <u>Pound</u>
1927 1929	3,200,747 6,760,000	\$ 472,508 876,000	.148 .130
1931	4,787,000	468,000	.098
1935 1937	5,873,943 7,982,056	668,282 1,072,395	.114
1938	7,274,653	909,486	.125

Source: National Farm Chemurgic Council, February 10, 1941

Once again, because of a shortage of metals, there is a national trend toward a wider use of wood in airplanes, military truck bodies, hangars, factory buildings, etc., "with an almost automatic corollary trend toward using casein glue. The whole renaissance of woodworking looks like a bonanza" (1) for the casein industry.

# C. Kind of Casein

While glue can be made from any of the commercial caseins, uniformity in the properties of the casein from

<sup>1.</sup> Business Week, "Casein at the Bat: Product of Many Uses," p. 104, Sept. 12, 1942



shipment is necessary, since changes in the glue formula are necessary with different types of casein. A medium to low content of ash is preferred, for the proximate ash content is a fairly reliable index of the relative viscosity of the glue made from it. Also the working life of the glue tends to be shorter the higher the ash content of the casein. Caseins made by different methods of precipitations are never blended in making a first class adhesive. Casein glue is made in many strengths, broadly classified as veneer, joint, and universal.

### D. Forms of Casein Glues

Casein glues are put on the market in two forms, prepared glues and wet-mix glues.

The prepared glues are sold in the form of dry powder containing all the necessary ingredients, except water. The user usually adds the powder to water (usually two parts of water to one of glue) at room temperature, and mixes in a mechanical mixer. Even large batches can be mixed in less than thirty minutes, but once mixed, the glue must generally be used within a working day or less.

The wet-mix glues are made as required for use, using ground casein, water, and the additional chemicals called for by the formula.

The woodworking industry uses both types in



large quantities, for each type has advantages. The wetmix glues allow the use of certain desirable ingredients
that cannot be very successfully incorporated in prepared
glues. They make it possible to add the components in the
most advantageous order, and allow the casein to swell
thoroughly in water before adding the other reagents, which
brings it into solution more rapidly and uniformly. The
formula can thus be varied easily to meet any special requirements. This type of glue is usually less expensive
per square foot of glue line.

The prepared glues, however, also have advantages, for the purchase and storage of only one material is necessary, and only two components need be measured and mixed so that the need of a skilled operator is less necessary than when the wet-mix glue is used.

## E. Advantages of Casein Glues

Some of the advantages of casein glues are that they set very quickly and produce joints strong enough to be machined in a few hours and durable enough to last indefinitely under reasonably dry conditions. It is reported that joints made with casein glue have been subjected for forty hours to a high-speed vibration test without showing any loss of strength. Also the two adjoining surfaces of glue joints made with casein do not have to be finished



as precisely as those made with most competitive glues. Casein gluing can be done at almost any temperature above freezing as compared with the temperature of 70° F. and above demanded by many of the strongest synthetic and natural adhesives. This fact makes casein glue especially useful in an airplane assembly, for example, since it is frequently carried on out of doors.

Casein glue costs more than vegetable glue or soybean glue, but its greater water-resistance, plus the already mentioned ability to set quickly after a joint is made and to make stronger joints with the denser hardwoods, gives it an advantage over the vegetable or soybean glues. However, animal glues are more adaptable to gluing operations with shorter assembly periods, and to the gluing of thin veneers with fancy grains, because the penetration of an alkaline glue stains the wood. Blood albumin glue is even more water-resistant than casein glue, but the highly water-resistant formulas require hot pressing, thus limiting their use to plywood and veneered panels.

# F. <u>Disadvantage of Casein Glue</u>

One serious disadvantage of casein glue not shared by other adhesives is that it forms an extremely hard glue, and when such glued parts pass through woodworking machines, the glue line dulls the knives of the tools.



### G. Uses of Casein Glues

The furniture industry makes much use of casein glue, particularly if the product made may be exposed for appreciable periods of time to relative humidities greater than 80%. For example, furniture for export, particularly to the tropics, and that which is used in many parts of the South, profit by the use of casein glue. Likewise, furniture and toys to be used at times out of doors are made with this type of glue, and in the difficult gluing operations in making laminated bent work (such as in the rims of grand pianos) it finds favor.

The use of casein glues in the airplane industry is so important that the United States Bureau of Aircraft Production has formulated very rigid conditions for its manufacture. (1)

In the automobile industry it is used in military truck bodies and in the making of floor boards and trunk shelves. About three to ten pounds of glue are used in every automobile.

Plymetal, plywood with sheet metal glued on one or both sides, is usually made with casein glue, and wood veneer is frequently glued with casein glue on the surface of metal fire doors, elevator cabs, and any other places where fireproof construction is needed, but the decorative

<sup>1.</sup> Rural New Yorker, November 6, 1937



effect of wood is desired.

The use of casein glues is considerable in the sporting goods industry. One use, for example, is in building up the laminations in tennis racquets. Baseball bats are sometimes impregnated to some depth with casein glue under pressure and then treated with formaldehyde to make the surface waterproof and to prevent splitting of the wood.

The luggage industry also uses casein glue in the manufacture of trunks and hand luggage, both in the plywood now extensively being used, and for gluing the members together and for covering the surfaces with fabric or leather.

Also in the construction industry, the use of casein glue finds an increasing use, for "carpenters of tomorrow may work with gluepot and brushes instead of hammer and nails. We may even find ourselves living in houses built largely of paper, or woodpulp products and glue. When such houses materialize, they most probably will be stronger, cheaper and more resistant to fire, storm, and weather than most homes of today."

It is used in structural plywood for house sheathing and subflooring; interior plywood for wall and ceiling
panels, door panels, cabinets, and store fixtures; and ply-

<sup>1.</sup> Popular Mechanics, "A New Age of Glue," p. 402, September 1937

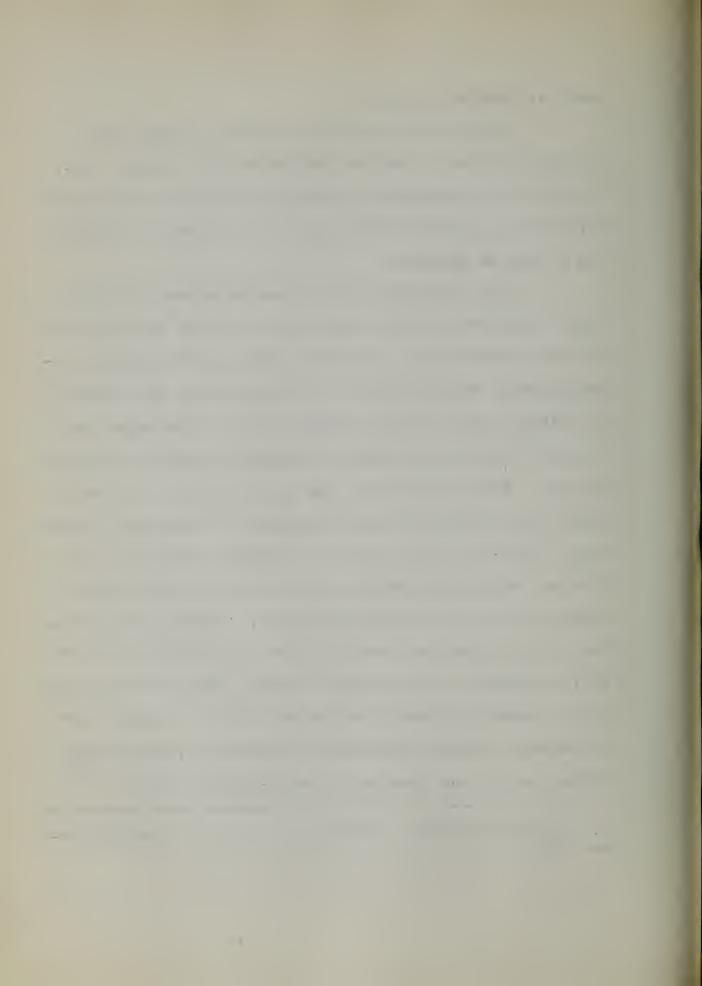


wood for concrete forms.

In the manufacture of millwork, casein glues are used for doors, built-in cabinets, stair parts, etc., for the water-resistance of the glue is desirable in woodwork being put in new buildings which are usually subject for a time to dampness.

One possibility for an increased use of casein glue in construction work may be as a method of fastening in wood construction. Laminated arches made by gluing together small strips of wood, or wood scraps, and pressing or molding them into any desired size or shape make possible the building of a modern commercial structure entirely of wood. Such arches have been used already in the building of the "Forest Products Laboratory" in Madison, Wisconsin. A 364-foot radio tower at Richmond, Virginia, and a 160-foot single span bridge over the Caddo River in California are also of this construction. "Perhaps the greatest of all structural uses for glues is developing in the prefabricated or factory-built houses, where various industrial builders are beginning to make use of assembly line efficiency and glue structure for increased strength and (1)better use of wood scraps and short-length timber."

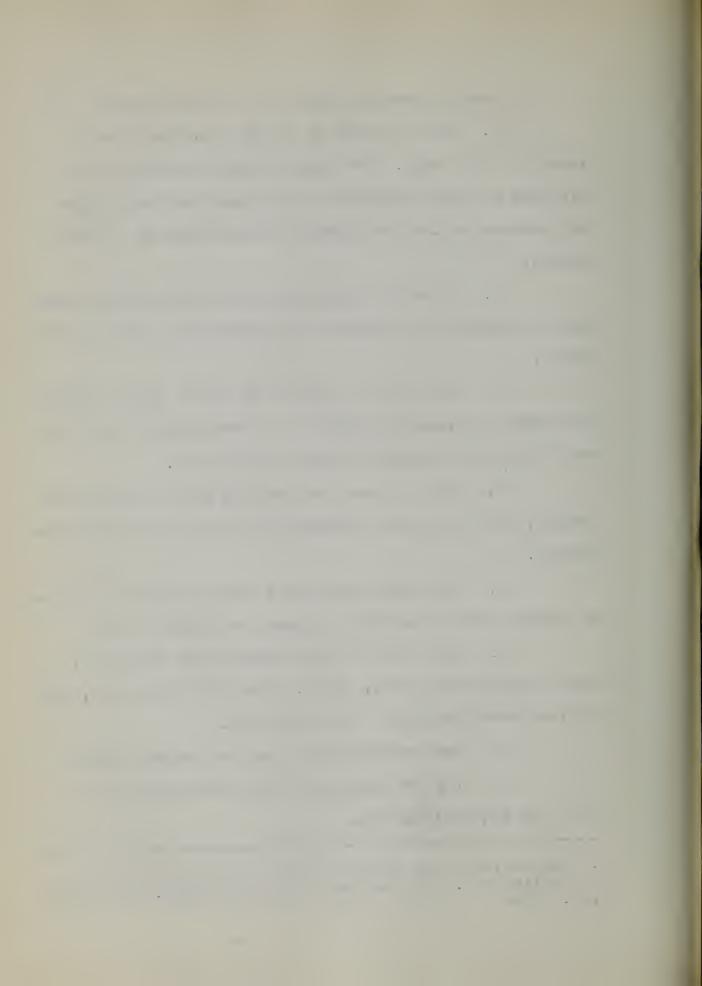
<sup>1.</sup> Popular Mechanics, "A New Age of Glue" p. 404, September 1937



Casein glues have many miscellaneous uses. (1)

- 1. They are used to attach linoleum to wood floors or table tops. The second largest market for casein glue was once reported to have been for use in gluing linoleum to the wood used for running boards in automobiles.
- 2. In making laminated safety glass casein glue makes a satisfactory adhesive for joining the glass to celluloid.
- 3. Mixed with a minimum of water, casein glues made seams in cigarettes that do not wrinkle and that will remain firm when exposed to humid conditions.
- 4. They are used for sealing paper bottles and cartons, and for pasting labels on glassware and metal containers.
- 5. Often they serve as a sizing material for use on shotgun shells and even for heels on ladies' shoes.
- 6. The binder in many composition materials, such as composition cork, tiles, mats, billiard balls, and linoleum substitutes may be casein glue.
  - 7. They are adapted to use in binding books.
- 8. They are employed in the construction of fruit and vegetable crates.

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications" p. 285, Reinhold Publishing Corp., New York, N. Y., 1938



A cement for stoveware, metals, porcelain, etc., may also be made from casein by dissolving it in a small amount of water and adding sodium silicate and calcium hydroxide in the following proportions: casein 100 parts, sodium silicate 5 parts, calcium hydroxide 5 parts.

An excellent putty can be prepared by adding finely powdered calcium hydroxide to a casein glue in sufficient amounts to give it a desirable plasticity. It hardens very quickly and is equal in good properties to other types of putty. (1)

<sup>1.</sup> Rural New Yorker, November 6, 1937



#### VII. CASEIN PLASTICS

### A. Early History

The first country to have discovered that formal-dehyde with casein produced a tough, insoluble, hornlike mass seems to have been Germany in about 1899.

In 1900 the rights were sold to France and the name Galalith, taken from the Greek meaning "milk stone", was established for the product. The two countries merged their interests and formed the "International Galalith Gesselschaft Hoff and Company." This pioneer company was the only successful manufacturer of casein plastic material in the world until the lapse of the basic patents and the World War made it possible for others to follow. It is still one of the largest producers, if not the largest producer in the world.

In 1909 a Russian student, Victor Schultz, patented a process for the manufacture of a solid plastic from milk curd and an English concern bought the patent rights and spent many years and much money to make a salable product, but not until the time of the World War, when some Irish capitalists became interested in the project, were they successful. The product was given the name of Erinoid, and for many years it was the most widely used casein

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 182, Reinhold Publishing Corp., New York, N. Y., 1938

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plastic manufactured in Great Britain. The Galalith Gesellschaft Hoff and Company also established a branch office in London.

The first successful casein plastic material to be developed in the United States was produced by P. C. Christensen about 1919 and was sold under the name Aladdenite. In 1924, Karolith was produced and soon Kyloid, Inda, and Erinoid. However, the process of manufacture was long and costly, and the material could not be worked advantageously in speedy automatic machines. (1)

Another difficulty was that the scrap, which in some cases amounted to 50% or more, could not be reworked, and since there was no profitable outlet for it, it was total waste.

Readjustment of the industry started in 1928 when George Morrell, a button manufacturer, took over the struggling Kyloid plant and prepared to make finished buttons from casein direct. Several other concerns soon merged their interest also, and the Button Corporation of America was formed. These companies do a large volume of business--over 8,000,000 gross annually--and there is good promise of an increase in volume, for they have been able to reduce and eliminate waste so that casein plastic buttons

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications," p. 185, Reinhold Publishing Corp., New York, N. Y., 1938

are able to compete successfully in the lower price (1) fields.

In 1931 several other small casein plastics merged to form the American Plastics Corporation and gave their product the trade name of Ameroid, practically the only American casein plastic raw material available to the trade as such. The major portion of this is sold in the form of button blanks, rather than in sheets and rods.

## B. Manufacture of Casein Plastics

In the early years of the casein plastics industry, a wet process of manufacture was used. George H.

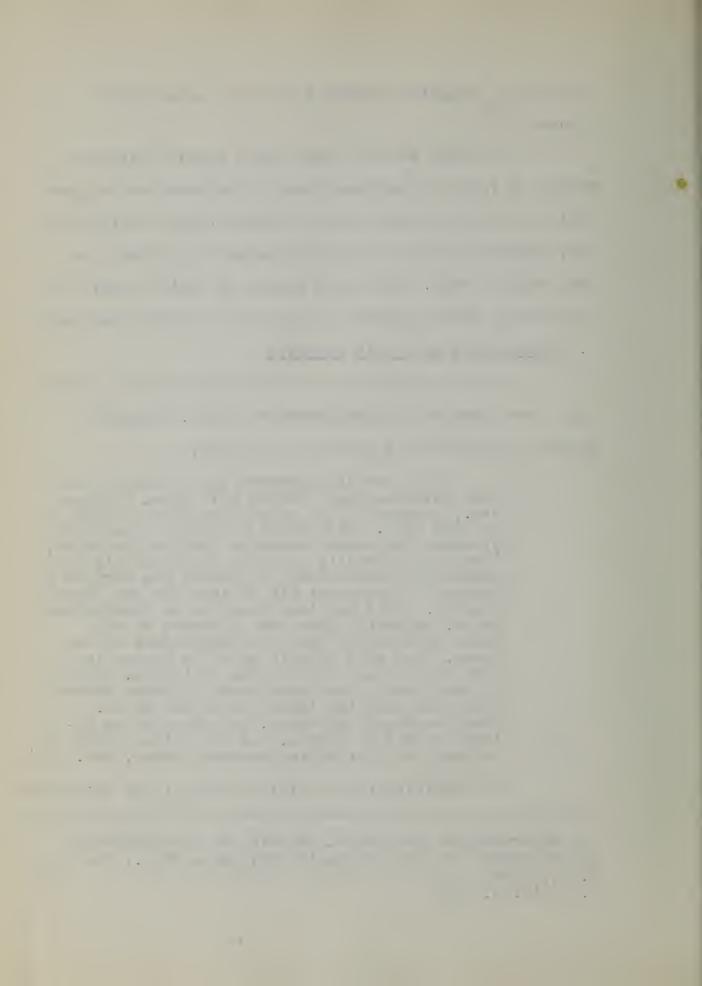
Brother describes this process as follows:

"Acid casein dispersed in an aqueous alkaline solution, and treated with dyes, fillers, etc., as desired, is coagulated with an acid or an acid salt. The curd is pressed at moderate pressure to remove the major part of the water, then in a hydraulic press at approximately 500 pounds per square inch to convert the curd to a rubbery, translucent (if fillers are not added) This may take from one to twenty-four plastic. hours, depending upon the thickness of the sheet desired and upon the temperature of the press. The soft plastic sheet is placed in a bath of aqueous formaldehyde to harden, where it must remain for three weeks to three months, depending upon the thickness of the sheet. When thoroughly hardened, the material is allowed to dry or season, and it is then ready to be used for fabricating buttons, beads, etc." (2)

Two modifications of this process later eliminated

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 185, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Ibid. p. 186



the long hardening treatment. One of these has the casein dispersed in aqueous ammonia, and formaldehyde solution is used as the coagulant. The other has the casein suspended in water and treated with acetaldehyde and an organic acid. Alkali is the coagulant in this method. The pressed coagulum hardens without the long formaldehyde bath and only the seasoning is necessary before it is ready for application. (1)

A dry process of manufacture is the newer and improved method, producing a less brittle material than that produced by the wet process. Rennet casein is the type usually used in this dry process and Mr. Brother points out that,

"It is essential that only pure, sweet, practically fat-free skim milk be used in the manufacture of rennet casein for the plastics industry.....The product should be granular, of light straw color, practically tasteless and with a very faint, pleasant odor.......According to Simmons, the best rennet casein for the manufacture of casein plastic material is produced in France, especially in the Department of Charente-Inferieure. In the United States at the present time there are three principal producers: Casein Manufacturing Company, New York City, Dairy Products, Inc., Chicago, and the National Casein Company, Chicago." (2)

If the casein has not been ground at the factory,

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 186, Reinhold Publishing Corporation, New York, N. Y., 1938

<sup>2.</sup> Ibid. p. 187



the grinding to pass a 40-mesh sieve is the first step in the dry process of manufacture. Next water is added, the percentage depending upon how the plastic is to be worked. The more water that is added the softer the plastic will be and the greater the shrinkage on finishing. Acid dyes are dissolved in the water before adding it to the water if the material is to be colored.

Many substances which are intended to act as plasticizers are sometimes added during the mixing. Mr. Brother questions whether in the present method of manufacturing, these substances accomplish their objective. He says:

"Water alone plasticizes the powder adequately and the long soaking in the hardening bath tends to remove the added substances, which are soluble in water, or so to modify their action that it is doubtful whether they are beneficial to the finished products." (1)

Application of pressure at elevated temperature is necessary for the conversion of the powder to the soft plastic and "in order to insure strength in the plastic there must also be mechanical working in such a way as to force the material to flow 'onto and almost into itself' by shearing, smearing, or some similar action involving flow throughout the mass." (2) Such devices as the heated

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 190, Reinhold Publishing Corporation, New York, N. Y., 1938
2. Ibid.



cylinder press with rotating screw, steam-heated kneading machines, and rolls with considerably less differential than when used for milling rubber are used for this purpose.

Next comes the hardening, the most critical and the most expensive step in the manufacture of casein plastic material. This process is essentially a reaction between casein and formaldehyde so it is necessary for the formaldehyde solution to penetrate completely the casein mass. Considerable time is needed for this step, varying from one week to six months depending upon the thickening of the mass. Other agents or methods have been tried as substitutes for this formaldehyde bath, but to date none have proved to be commercially important.

After the material is hardened, it must be seasoned or dried, a process requiring about the same length of time as the hardening, for the excess water and formal-dehyde have to be "expelled without rupturing the material or setting up stresses and strains within it."

# C. Improvements in Manufacturing Techniques

In 1929, Christensen found that the incorporation of about 2% of a water-soluble aluminum salt in the soft

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 190, Reinhold Publishing Corporation, New York, N. Y., 1938
2. Ibid. p. 198



plastic gave a material rigid enough to be worked in automatic machines and yet be easy enough on the cutting edges of the tools to prevent their ruin. Before this, much hard labor had been required to make buttons and dress ornaments, and this made the cost of production far too high. A special machine had to be designed to turn the rods directly into buttons, and since this machine could be geared to a very high speed, mass production became possible.

The addition of the aluminum salt also made the scrap material reworkable, so practically no waste ensued, and since the buttons made by this method were bathed after being formed, the time required for the penetration of the formaldehyde was only three to five days, as compared to one week to six months by the previous method. The thinness of the formed buttons accounts for the time saving.

With all these reductions in the cost of production--saving in overhead and labor cost and elimination of waste--the business has steadily grown, but the button industry is still looking for ways to reduce further these items. Attempts have been made to utilize profitably the waste as a filler for other plastics, fertilizer, or as a base for the preparation of lacquer, but none has been too successful, the best method seeming to be the elimination of the waste as far as possible.



A new method of polishing plastic material has proved money-saving and helpful, for it increases the water-resistance of the material, makes it less subject to losing its lustre and polish when in contact with surface dampening, as for example, handling with damp hands or frequent washings, and less subject to scars or scratches when rubbed against itself or materials harder than itself. Since most cleaning and pressing establishments in the United States use the steamed clothes press, such improvements have proved helpful to a successful use of casein plastic.

Considerable progress has been made recently, according to the 1941 "Modern Plastics Catalog" in the development of new colors and color effects. Colorability is one of the outstanding properties of casein. The fact that it is non-inflammable is valuable also.

## D. Weaknesses

The most serious weakness of casein plastic material is the readiness with which it absorbs water. Although this tendency is checked to a great extent by the hardening reaction, it eliminates it from a number of fields and seriously restricts its application in others. "The material not only absorbs moisture if soaked in water, but it also "breathes" with changes in relative humidity of the



air," (1) so for example, casein plastic material is unfit for use in combs in the United States, where there are sudden temperature and humidity changes in many parts and extreme variation from one place to another. Such a use (in the manufacture of combs) is a large outlet in Europe, however.

Large panels or long rods of plastic casein would warp badly because of the sensitivity to humidity changes, and the same situation would be true where accurate dimensions are required, such as for sliding or friction fits. This defect, together with the tendency to loss of polish by surface fractures caused by handling, practically eliminates its use in the pen and pencil field. Its use in the electrical field because of this defect has been entirely restricted to interior insulation, and even here its use is limited, for while it is an excellent electrical insulation, only a small absorption of moisture causes its dielectric constant to drop sharply.

Emphasis, therefore, in recent research is being directed to finding plasticizers, which will reduce the hygroscopicity of the material and increase its elasticity or pliability. Such agents as aluminum stearate, or ther-

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications" p. 212, Reinhold Publishing Corp., New York, N. Y., 1938

moplastic formaldehyde-hardened soybean protein have proved somewhat effective.

### E. Extent of Use

The amount of casein used in this industry is now very sizable and is continuously increasing. Dr. George H. Brother, Senior Chemist in the United States Regional Soybean Industrial Products Laboratory in Urbane, Illinois, offers these comments concerning its growth:

"There was practically no production in 1931 of these casein plastic buttons and 1170 tons in 1935, nearly the total amount of casein plastic consumed by the whole country in 1931. In 1938, the total production must be between 4000 and 5000 tons annually."

War shortages have accentuated the demands for plastic products, including casein plastics. "Essential parts of our airplanes are being made of these newer synthetic materials--fuselages, gun-turrets, observation 'blisters', shatterproof windows, radio masts, fluorescent plastic instrument boards to aid night flying." (1) Synthetic resins take the place of scarce metals, thus releasing them for more essential defense tasks.

Charles A. Breskin has said that "today plastic things have ceased to be mere novelties. They are doing an essential job in these critical days. In one bomber,

<sup>1.</sup> Science News Letter, "Plastics in Defense", p. 314 November 15, 1941



for example, the nose section of the fuselage is made not of the conventional aluminum but of plastic plywood, studded by transparent plastic windows. In addition to releasing aluminum, the laminated mahogany veneers bonded with plastic save 15% in weight with no sacrifice in strength and the rivetless surface through its smoothness results in increased speed. Mass production is speedier and cheaper."

Small but essential parts of airplanes once made of metal are now being made of casein and other plastics, such as radio masts, ventilators, and vital control aileron pulleys. There is not only a saving of weight and cost but also a gain in time of production since the plastic parts can be molded ready finished without any time-taking machine work.

Many parts inside the plane are now also being made of plastics, as, for example, the instrument panels, housings for the instruments, and luminous dials for them, as well as innumerable handles, knobs, and switches. "Panels that glow in ultraviolet or 'black' light allow the pilot to see but are invisible to the enemy."

The tanks that hold the gasoline are made self-sealing by plastics.

Often the clothes, helmets and gloves of the aviators are

<sup>1.</sup> Science News Letter, "Plastics in Defense", p. 315, November 15, 1941
2. Ibid.



composed in part of plastics and plastic textiles.

On the European continent casein plastics had long been successfully produced, but only in the last few years has the United States plastics industry forged ahead. limited only by raw processing materials and plant equipment, into a multitude of remote and distinctive uses. The beer cans used for the Army have a thin plastic lining to protect the tinned steel from the beer and vice versa. In blackouts, fluorescent materials placed in the transparent plastics, will radiate mild light under the influence of invisible ultraviolet illumination. Irreplaceable metal formerly used in furniture and equipment, telephones, cash registers. calculating and accounting machines, lighting fixtures, lampshades and reflectors, radio and musical instruments, scientific instruments, etc., is being replaced now by plastics. An excellent artificial celluloid may be made from plastic casein. It is practically noninflammable and has almost as much elasticity and tensile strength as pure celluloid.

Casein combined with various other substances forms materials for making excellent grades of artificial jewelry. Ebony or jet may be made by mixing casein with lampblack or various mineral blacks; jade or lapis lazuli, casein with powdered malachite green or aniline green;

0 = ( . 0 = 0) gold stone, casein with powdered brass or bronze; amber, casein hardened with picric acid; and silver stone, casein with powdered aluminum.

<sup>1.</sup> Rural New Yorker, "By-Products of the Dairy Industry" May 8, 1937



#### VIII. CASEIN FIBRE

## A. <u>Historic Development</u>

The first practical attempts to spin casein filaments were carried out in Germany by Dr. J. C. Todtenhaupt. The fibres were produced by dissolving dry casein in a suitable solvent, probably dilute sodium hydroxide, but they did not resemble wool because they were hard, brittle, and of poor durability.

Italian chemist, investigated this problem of transforming the still unsalable German product into a pliable synthetic fibre with the properties of wool. At the end of his study the largest Italian rayon concern, "Snia Viscosa", bought his patent and began to produce artificial wool on a large scale basis. The fibre was named Lanital, a contraction from lana Italiana, or Italian wool. Dr. Ferretti's knowledge of the technique of the manufacture of rayon greatly aided him in his work on Lanital, for the two processes are very similar, and after some initial failures, "a supple wool-like fiber, with a pleasant lustre and considerable crimp, with a firmness corresponding to an A/B wool was produced."

The process used by this large company is briefly

<sup>1.</sup> Textile Colorist, "Casein Fiber", p. 385, June 1938

order to the term of the second secon  to add water and certain solvents to the casein, thus producing a viscous substance, which is then forced through spinning nozzles in which there are a large number of holes from .02 to .03 mm. in diameter. The fine threads leaving the nozzles pass into a bath of hot sulphuric acid in which they are coagulated and hardened, and then the acid in the fibres is neutralized by passing through an alkaline bath. The bundles of fibres then are cut into short lengths, forming "flocks" and these "flocks" are finally immersed in a bath of formaldehyde in which they are allowed to remain 10 to 15 hours. After drying in steam heated drying machines the material is ready for spinning and weaving into fabric by the usual processes.

The keen interest that Italy has in the development of this new fabric was shown when at the Mostra del Tessile Nazionale, a pavilion was devoted entirely to Lanital, showing the whole process from the milk to the finished product. Of course, sanctions applied against Italy by the League of Nations around 1935 gave increased impetus to the attempt to produce artificial fibres.

In 1936, the Italian output was 300 tons and in 1937 a new plant was started which would be able to produce 25 tons of Lanital daily. Italy's capacity to produce, however, is limited by her supply of casein, which before the

 War was about 9850 tons per annum. She supplemented this amount by large imports from Holland, Denmark, and Argentina. In 1940, a trade report of Snia Viscosa's annual meeting indicated that their total output capacity was 30,000,000 pounds per year and their casein supply was 15,000,000 pounds per year.

"Snia Viscosa has been doubling its lanital plant at Cesano Maderno, which indicates constantly increasing use of the product."

(2) This company granted licenses in Canada, France, Belgium, Holland, Poland, Germany, Czechoslovakia, and Japan, and also had a joint Dutch and Italian corporation.

# B. American Fibres

In December of 1937, the United States began importing lanital through the American agents of Snia Viscosa, and in 1938, Stephen P. Gould and Earl O. Whittier, of the Bureau of Dairy Industry, United States Department of Agriculture, devised a process for making from casein a synthetic fibre, having the appearance of wool. The process differs somewhat from the Italian one and was perhaps an improvement over it, in that it can be applied to casein obtained from other than cow's milk.

<sup>1.</sup> Atwood, F. C., "Natural Protein - Base Spun Fibers", American Dyestuff Reporter, March 17, 1941
2. Ibid.

<sup>3.</sup> Science 89-Sup. 12, April 7, 1939, "Milk As a Raw Material for Industry"

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The chemical composition of this new synthetic fibre is almost identical with wool, (see Table II, page except for a lower sulphur content. It is faintly yellow in color and closely resembles best grade, thoroughly washed and carded, Merino wool, the finest size marketed. The casein fibre has also the characteristic fine kink of natural wool and may be blended with it to make a product that has the resilience of pure wool.

(1) Paul LaRose describes this casein wool in an article in the Canadian Textile Journal as follows:

"In tough the fibres are somewhat softer than a fine wool top. Under the microscope the longitudinal view of the fibres is very much like that of certain rayons. There is no twist, the fibres appearing as smooth cylinders covered with a multitude of fine circles or dots and longitudinal streaks, probably due to air bubbles trapped in the fibres. In the cross-sectional view the fibres appear almost circular. Some of the fibres show indentations which, however, are not as pronounced as in some of the rayons." (2)

while synthetic fibres with this kinky structure have been made from plant materials, it was found that they will not take wool dyes, while casein fibre will dye more easily and more evenly than wool. However, the temperature at which it is dyed should not exceed 70° C., for the fabric becomes weakened if exposed to temperatures near or above the boiling point, and such loss of strength is never regained.

<sup>1.</sup> Scientific American "Wool-Like Fiber from Skim Milk", November, 1938

<sup>2.</sup> LaRose, Paul, "Casein Wool", Canadian Textile Journal, p. 45, April 17, 1936



Since the fibres are smooth, rather than scaly like natural wool fibres, they cannot be felted. For this same reason, however, the synthetic fibre does not shrink as much as wool.

Perhaps the greatest defect of this synthetic fibre is its great loss of strength when wet, the percentage of loss being between 50 and 60. While this strength is regained on drying, this artificial fibre is never used alone, but always in mixture with natural wool, the wool usually equalling the amount of synthetic fibre and often being considerably in excess.

Some advantages of it are that it has high resistance to creasing, is not susceptible to moths, and is as warm as wool. By varying the acid bath in the manufacture of it, the fibre may be made either soft or hard to the touch. The softer grades, while not as strong, make up into knitted garments which can be worn next to a sensitive skin that cannot tolerate knitted wool.

In 1937 also, the National Dairy Products Corporation began to search for chemurgic or industrial uses for the by-products of the milk industry and started a serious investigation of the possibility of producing a fibre from casein. Inside of a year plans were begun on an experimental plant at Bristol, Rhode Island, to produce 1000 pounds



per day. This plant started operation early in the summer of 1939. Sample lots of fabrics were made and tested for resiliency, tensile strength, abrasion, odor, affinity to dyes, and ability to withstand dry cleaning and washing.

Finally on November 8, 1941, the National Dairy Products Corporation announced to the public the commercial production of "Aralac", a protein fibre, made from casein. The name is a combination of the first initials of Atlantic Research Associates, Inc., and lac, the Latin word for milk. A new plant was opened at Taftville, Connecticut, by Aralac, Inc., a special manufacturing division established by National Dairy Products Corporation.

All the casein which is sent to this factory is carefully blended in large lots prior to use, so that a uniformity of raw material is insured just before the manufacture of the fibre. Then the blended casein is carefully dispersed or dissolved in water with suitable solvents, involving proper adjustment "of the viscosity to a uniform base and adjustment of any other factors including complete removal of heterogeneous aggregates or any adventitious material and certain other adjustments are required to insure clean, continuous spinning over long periods of time in substantial volume."

<sup>1.</sup> Atwood, F. C., "Aralac", American Dyestuff Reporter, p. 156, Vol. 31, March 30, 1942

Next through spinnerettes the dispersed syrupylike casein is forced into a coagulating bath. In a large wet tow the regenerated casein, as fibre, is collected and carried away from the coagulating bath. In this tow form it remains through a succession of hardening and molecule modifying treatments interspersed at times with washing and drying, together with surface modifying treatments. The use to which the finished fibre is to be put determines and varies the number and sequence of the steps in the treatments which serve to change the casein molecule into a new resin compound. It is not until the shipping department receives an order for the fibre that a selection from inventory is made and the tow receives its final treatments and conditioning and is put through cutting machines to yield the desired length of staple. This cut staple is then carried through suitably designed openers and blowers from which it goes into large blending rooms for final conditioning. Here sufficient material is blended and the fibre is taken from the room in such a way that the equivalent of another blending is insured before it is dropped into a baling press and is finally prepared for shipment.

It is substantially true that any diameter fibre may be made, but Aralac, Inc., has found that the quality

<sup>1.</sup> Atwood, F. C. "Aralac", American Dyestuff Reporter, Vol. 31, March 30, 1942

and character of Aralac is such that products made "with a fibre diameter distribution substantially equivalent to 50's, 60's, and 70's wool or 30, 25, and 20 micron diameter on the average covers the principal uses in which Aralac has been successfully used to date."

(1) However, they have made as small as 9 microns and as large as 400 microns.

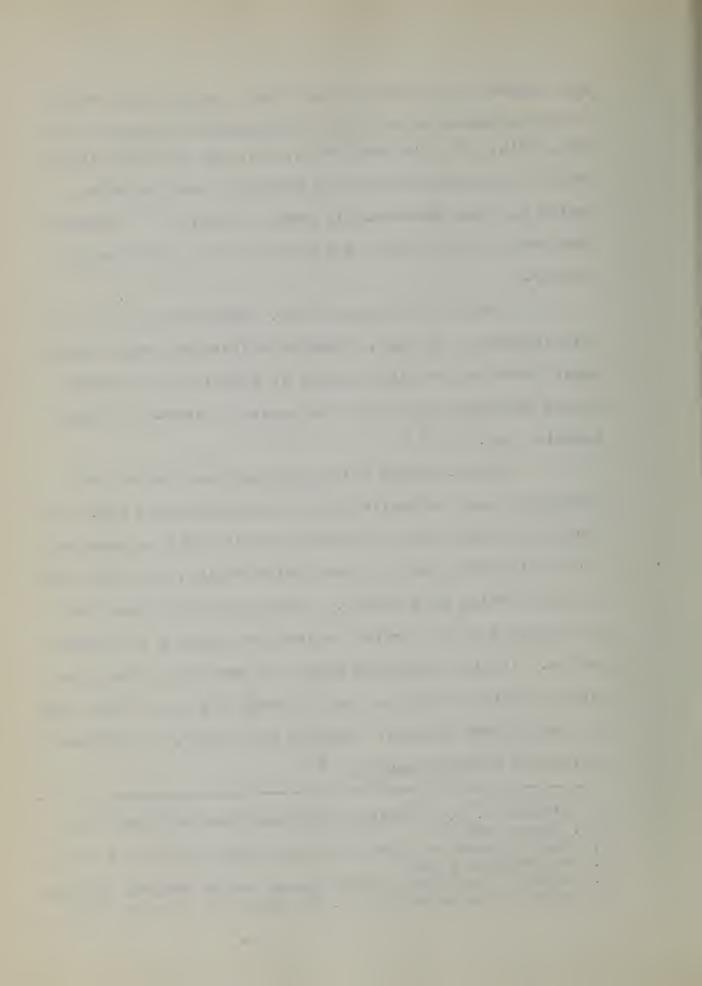
Aralac has several uses, especially in the textile industry. In fact, "fashion writers may soon inform their startled feminine readers of bargains in perfectly divine Guernsey cow prints and Holstein jackets of unmistakable chic."

Aralac blends well with rayon and cotton and provides a more versatile fabric for year-around use. For example, a 100% rayon or cotton garment might be uncomfortably cool during the fall and winter months, but the blending with Aralac adds warmth. Perspiration and body heat are absorbed by the Aralac in the blend during the summer months. It also "supplies drape and substance which previously could be obtained only through the use of wool and fur and in some fabrics. Blended with rayon, it produces fabrics of unusual beauty."

<sup>1.</sup> Atwood, F. C., "Aralac", American Dyestuff Reporter, Vol. 31, p. 156

<sup>2.</sup> Modern Plastics, "Textiles from Casein Protein Fiber", p. 38, December 1941

<sup>3.</sup> Rayon, "New Casein Fiber Aralac Now an Assured Success in Textile Manufacturing", p. 34, Vol. 22, November 1941



In combination with rayon or rayon and cotton, it also adds resilience, warmth, and absorbability to knitting yarns for use in anklets and men's half hose.

Aralac blends remarkably well also with wool, since they are both protein fibres. Not only can fine wools be used, but when blended with coarse grades, it produces "a softer, grander-appearing fabric. This blend assures a crush-resistant, easy-to-tailor, dry cleanable cloth. There's a natural resilience which guarantees permanence of fashioned-in features and discourages wrinkling or sagging."

One of the first uses of Aralac was in combination with wool in ladies' hats and with fur in men's hats. In the course of a twenty-year search by National Dairy Products Corporation for a fibre that could be used in making top-quality felt hats, numerous fibres were tried, such as "Texas Wool, Super China Lamb's Wool, Vegetable fibre, fast shrinking wool, de Laine Wool (Botany Quality), Viscose Rayon Staple (dull and bright), Acetate Rayon Staple, Fiberglass, Nylon Staple, Venyon Staple, Cotton, Ramie, Lanital (Italian casein), Enkasa (Dutch casein), and Japanese casein, all of which did not meet the specifications and requirements."

<sup>1. &</sup>quot;Aralac", Pamphlet issued by Aralac, Inc., p. 5
2. Rayon, "New Casein Fiber Aralac Now an Assured Success in Textile Manufacturing", p. 30, Vol. 22, Nov. 1941



Aralac was tested and it proved satisfactory. The name "R-53" was given to it, for it was the 53rd fibre tested and the "R" stands for "Research".

Although "R-53" is of the same basic material as Aralac, much additional processing is necessary before the fibre is ready for hat making. Much combing is needed, for example, to remove knots and to make a straight fibre, for the rabbit and beaver whose furs are used in the making of hats have straight hair. It must also be cut to the proper staple length,  $\frac{3}{4}$ ", for blending with the fur. Wool, on the other hand, is a crimpy fibre, so when the casein fibre is to be blended with it for wool felt hats, "some corkscrewy ideas have to be put into the Aralac."

Popular science writers, reporters, and publicity departments have frequently referred to the National Dairy Products Corporation as magicians who have pulled the rabbit from the hat, but Dr. Atwood remarks that if "you ever see rabbits being pulled from hats, just remember the rabbit must have been placed there first,"

(2) and by use of "R-53" there is actually a prevention of the rabbit's getting into the hat.

Men's hats are and always have been made of fur, and it is the scarcity of high-grade hat making fur that

<sup>1.</sup> Atwood, F. C., "Chemurgic Products from Milk", p. 8, June 19, 1941

<sup>2.</sup> Atwood, F. C., "Rabbits from Hats", p. 5, March 26, 1941

makes high-grade soft and supple hats expensive. The beaver from the United States and Canada, the nutria from Argentina, the hare from Continental Europe, and the rabbit or cony from England, Scotland, Australia, and New Zealand are the chief source of furs used for felting, a process "which is supposed to have originated when some ancient sheep herder observed the matting or felting together of sheep's wool which had been placed in his shoe as a pad under his foot. The wool was subjected to moisture, to heat, to motion and pressure. Those same conditions are still required to make felt."

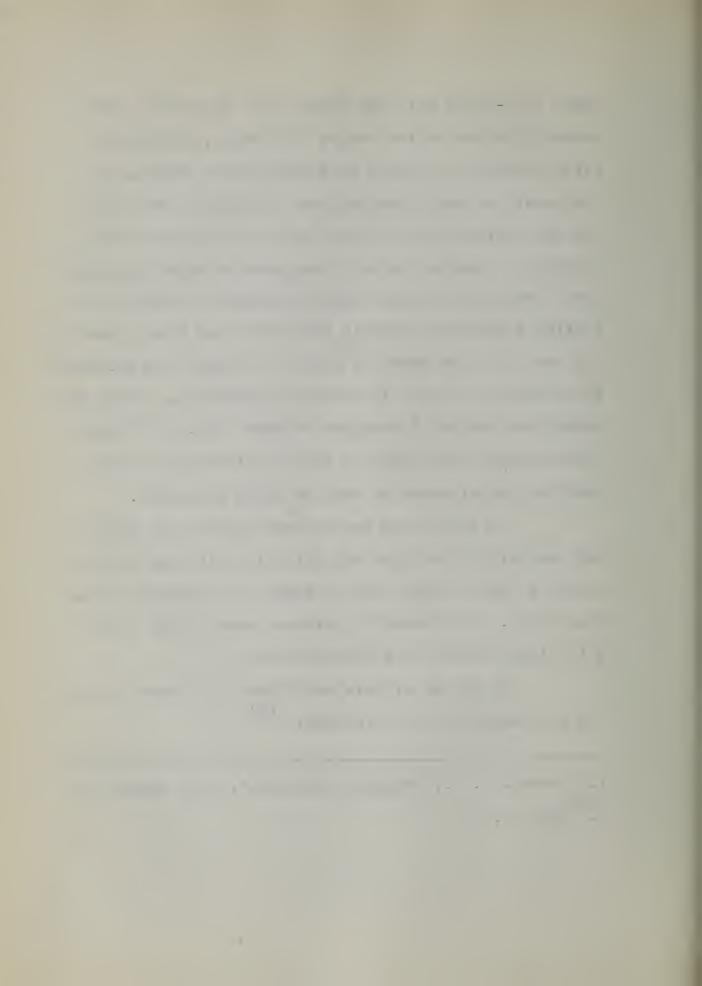
Thus the milk-made fibre must be able to withstand all the exacting requirements of each of these processes.

It takes from two to three rabbits to make a hat, so only if and when the milk fibre is used to the extent of 30% or more would a rabbit be actually pulled from a hat. At present the mixture used is 10% to 15% milk fibre and 90% to 85% natural fur.

In praise of this new fibre, Dr. Atwood quotes one hat manufacturer as follows: (2)

<sup>1.</sup> Atwood, F. C., "Rabbits from Hats", p. 5, March 26, 1941

<sup>2.</sup> Ibid. p. 8



"The new felting process represents the first time in the history of fur felt hat making, from the legendary St. Clement to the present day, that any fiber other than fur has been used in the volume production of regular finishes.....Among the qualities which make the new fibre specially applicable to hat manufacture are its fine diameter (about the same as fur); its specific gravity, which again is similar to fur and aids thorough distribution in blowing and forming; its affinity for dyes; said to be even greater than that of fur: its acidity, texture and moisture content, its quality of shrinking as the hat body is sized -- and. of course, its availability of supply. There is also the consideration that, unlike fur, it can be standardized, and cuts conveniently to threequarter inch lengths. It is stated to be particularly resultful in suede finish types, producing a silkier surface than the all-fur hat."

It is claimed that the addition of casein fibre makes women's wool felt hats softer and better to handle.

The finished felt has a "'marvelous silky mellowness, hitherto unattainable.' "

(1)

Shortly after the first sample hats were submitted to the Army for test, new specifications were issued allowing the use of Aralac, so now many Army hats are made in part of this product.

Aralac may also be used alone for interlinings

(either batted or woven) and in batt form, as a light,

warm filling for comforters and pillows. With the present

scarcity of down, Aralac offers a welcome substitute.

<sup>1.</sup> Atwood, F. C., "Rabbits from Hats", p. 9, March 26, 1941



Dr. F. C. Atwood, Vice-President of Aralac, Inc., estimated that by the end of March 1942, there would be in process some six to ten million yards of fabric containing a percentage of Aralac, the percentage running from 20% to 50%, depending upon the class of goods and the price for which it is to be sold. (1) Ever since casein fibre has emerged from an experimental to a commercial scale of manufacture, it has been selling for \$.64 per pound, and the felt (for hats) has been selling for \$.74 per pound. (2) While this is more expensive than rayon and cotton, it is much cheaper than wool and fur, so that the public will be able to buy a fabric having many of the advantages of the more costly materials at a lower price.

A non-textile use of Aralac is Wave Crepe, a lanolin-treated wrapping fibre, for use with permanent wave machines instead of the fine, natural English wools formerly used. Aralac, Inc., advertises that it will take "top heat, is completely free of scales, assists in treating abused hair, and it's easy to use."

Despite all the good points of Aralac, it is still a protein fibre. It is not cellulose, like cotton, viscose or acetate. In sizing, scouring, bleaching, stripping or dyeing, it should be treated with at least as much

Atwood, F. C., "Dairy Chemurgy", March 25, 1942
 Information received from Atlantic Research Associates,
 Inc., Newtonville, Massachusetts



respect as would be accorded to wool or silk in all reactions and treatments. The same is true of dyeing and drying temperatures. The milk fibre is still a bit below the natural protein fibres in ability to stand rough wet treatments. Since Aralac will be found in many combinations with cotton and rayon, it is suggested that the original tints be light so as to avoid stripping problems. (1)

Dr. Atwood was hopeful that by the middle of the summer of 1942, 1,000,000 pounds of Aralac per month could be shipped. The present production capacity of Aralac, Inc., is about 5,000,000 pounds a year, the recoverable casein content of approximately 160,000,000 pounds of skim milk. The factory is now operating on a 24-hour basis. (2)

<sup>1.</sup> Atwood, F. C., "Aralac" p. 158, American Dyestuff Reporter, Vol. 31, March 30, 1942
2. Ibid.



### IX. CASEIN IN THE LEATHER INDUSTRY

# A. Type and Extent of Use

The use of casein in this industry is confined almost entirely to the last of the finishing operations, which consist in coating leather with certain preparations and then subjecting it to mechanical operations, such as glazing, plating, brushing, and ironing. Such a process is called seasoning.

In this process casein is used in admixture with other substances, for it alone does not possess all the properties necessary for giving the final characteristics and appearance to leather. Often, in fact, it is but a minor ingredient of the seasoning, acting as an emulsifying agent.

The use of leather in clothing has shown a marked increase in recent years and a wider variety of colors and finishes is necessary. These are obtained by use of seasoning materials or pigment finishes, which also supply a finish resistant to water. Casein has proved effective in securing these results. One example of casein used in leather would be the top finishing of hat leather, which requires that the finish be highly water-resistant, because of its constant contact with perspiration.

Quite an amount of casein is also used in the manufacture of pigment finishes. Sometimes it is used for



clarifying vegetable tanning solutions, as an ingredient of the paste used in pasting leather, and as a waterproof glue used to cover machine rolls where wet leather is used.

B. Kind of Casein

For a long time Argentine casein was imported for the leather industry, and since that was a lactic casein, the leather trade still seems to prefer this type of casein, although the most important requirement of the casein used is uniform viscosity of the solutions made from it. It serves as a filler and a good binder, increasing the ability of the seasoning mixture to bind or glue it more tightly to the leather. "Owing to the relatively large micellar weight of casein, it does not penetrate too deeply into leather, and when used in a mixture, it acts as a protective colloid, in that it prevents other ingredients from being selectively absorbed by the leather." (1)

Perhaps the chief drawback to its wider application in this industry is its tendency to be brittle. Some effective method of plasticizing casein would be necessary to overcome this defect, for a great many leathers must withstand a great deal of flexing and stretching. Any film

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 382, Reinhold Publishing Corp., New York, N. Y., 1938

applied to the surface must be as flexible as the leather itself, but it also must be hard. Casein answers the last requirement, but it will break up in many tiny cracks if flexed much.

Oils and glycerol are often incorporated in the casein solution to lessen this brittleness and some improvement is effected.



#### X. CASEIN IN FOODS

### A. Special Diets

The casein protein has its main use in the food industry in the manufacture of cheese, but casein also has proved useful in other food products, especially answering needs in the nutrition of infants, the sick, the convalescent, and in dietotherapy of diabetes. For these purposes a high-grade casein, purer than the ordinary industrial casein, made by a grain-curd process, developed by W. M. Clark and some associates, is used. (1)

One of the earliest of these milk foods appeared on the German market several years ago and was called Guttmann's Nutrient Flour. The base is skim milk casein, and it is reported to be very digestible and especially adaptable to the needs of children and of dyspeptics. In the form of powdered skim milk casein enters into the composition of several proprietary foods used for infant feeding. Sometimes casein itself is used, "being modified to a certain extent by the introduction of substances like the phosphates, or precipitated in a way to render it substantially ash-free."

Casein enters also into malted milk, since it is

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 369, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Ibid. p. 371



a constituent of the milk from which it is made.

A product called "Lister's Casein Palmnut Dietetics Flour" uses casein in its formula, as do several other formulas for diabetic food.

### B. Baking Industry

To a limited extent casein is used in the baking industry. Dry skim milk, for example, has been found to have beneficial effects upon the volume of the loaf and the texture of bread, if it is incorporated into the dough-mix in quantities not exceeding 6% of the weight of the flour used. Curdolac-Casein-Bean Improved Flour contains casein. This flour is used for making muffins or bread of low carbohydrate content or food value, but supplying bulk. There are other similar preparations on the market. Bakers also have used a skim milk product as an egg substitute. The skim milk is heated to 95° C., flour is added, and casein, containing also albumin, is then incorporated with it by precipitation. (1)

## C. New Uses of Whey

It is interesting to note that the National Dairy Products Corporation has been carrying on experiments to find further use of milk or its by-products

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 376, Reinhold Publishing Corp., New York, N. Y., 1938



and new ways to use whey are being found. To date it usually has been fed to pigs or thrown away, for although when completely dried into powder, it is marketable for use in feeding young children or in other diets where high-grade mineral content and easy digestibility are especially desirable, only a very small fraction of the total whey output was thus accounted for.

Under the instruction of Dr. B. H. Webb of the Bureau of the Dairy Industry, a half dozen forms of deliciously tempting candy have been made which have been found by tests made on animals, to be definitely less fattening than the kinds on the market at present. (1) While this candy is not now commercially obtainable, it is hoped that candy manufacturers will become sufficiently interested to undertake its large-scale production. It is made by adding 7% of ordinary granulated sugar to pasteurized whey, of which there is a vast quantity produced in creameries and cheese factories all over the country.

Two of the most successful forms of whey candy so far worked out are fudge and caramels, in which whey constitutes nearly half the total weight of ingredients.

A new piece, however, has been innovated by Dr. Webb, which he calls "Wheyfers", a crisp and crunchy candy somewhat

<sup>1.</sup> Science News Letter, "Whey to Make Candy", Feb. 1, 1941

like molasses chips, but without the hard texture which many persons find disagreeable in the confection. They are also entirely new in flavor, and most of those who have tried "wheyfers" are enthusiastic. (1) The Bureau of Dairy Industry "promises a time soon when you can finish a dinner with cheese and bonbons that both come out of a cow."

Of course, lactose, another by-product of milk, has been used for many years in making fondant, and its advantage seems to be that it prevents the too sweet criticism usually given chocolate covered creams.

Another use for whey devised recently is a pudding with less shortening and richness than plum pudding but more cake texture and sweetness than the canned breads. It has several desirable characteristics. Whey gives it a pleasant and distinctive flavor that cannot be obtained with other materials within the price range of whey solids. "The mild acidity of whey is of advantage since through the use of sodium bicarbonate, carbon dioxide is released for leavening. During processing of the pudding an attractive dark color is developed as a result of the caramelizing action of heat upon the lactose of the whey. Whey albumin

<sup>1.</sup> Science News Letter, "Whey to Make Candy", p. 74, Feb. 1, 1941

<sup>2.</sup> Ibid. p. 75



is effective in improving body and producing a cake-like texture in somewhat the same manner as does egg white."

There is a high nutritive value to the pudding, of which 22% of its solids, exclusive of fruits, is derived from whey.

The 1940 Byrd Antarctic Expedition gave practical recognition to the value of powdered whey, for they took along many specially prepared whey-containing foods, one example being a pea soup made with whey powder.

Still another very recent experiment the National Dairy Products Corporation has been carrying on is the making of Sherry and Sauterne wines from milk.

### D. Wines

Since "Asiatic tribes, known as Kumanes or Kumans, made a 1% to 2% alcoholic beverage from mares' or camels' milk, and today, as they have for centuries, the Siberians and Caucasians ferment milk to make kefir, a 1% alcoholic drink,"

(3) the making of wine from milk is probably as ancient as the use of intoxicants. However, the National Dairy Corporation gets more pep from milk than the ancients ever dreamed of, for its wines are 15% alcoholic.

<sup>1.</sup> Brown, H. H., "Canned Whey Pudding--A New Product", p.36 Food Industries, November 1941

<sup>2.</sup> Atwood, F. C., "The Dairy Industry and Chemurgy", p. 4, presented at the Second Mid-American Chemurgic Conference, September 16 and 17, 1941

<sup>3.</sup> Food Industries, "Wine Made from Milk", p. 59, January 1941



If such wines acquire commercial importance, the alcoholic beverage industry will benefit as well as the farmer, for the prohibitionist will have the dairy farmer also to contend with.

### E. Diverse Uses

A non-gelatinizing solution of casein is said to be able to emulsify and bind the fats and water of oleomargarine, giving it many of the properties of butter, such that it may be spread, and when heated becomes brown and will not splash.

(1) With the present scarcity of butter, there should be a considerable increase in the quantity of oleomargarine used.

Skim milk powder emulsified with butter fat is widely used in ice cream.

In Germany, particularly, casein is the major constituent in soup tablets, bouillon cubes, and other concentrated foods of that type.

Baking powder has as one of its constituents a casein phosphate preparation, and soluble casein sodium is sometimes added to cocoa.

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications, p. 376, Reinhold Publishing Corp., New York, N. Y., 1938

#### XI. CASEIN IN MEDICINE

### A. Cure for Liver Cirrhosis

Dr. Lowry, Dr. F. S. Daft, Dr. W. H. Sebrell, Dr. Ashburn, and Dr. R. D. Lillie of the U. S. Public Health Service report success in both treating and preventing cirrhosis of the liver with a B vitamin, and casein choline is believed to be one of the B vitamins so this with casein was given to patients by Dr. Arthur J. Patch, Jr., and Dr. Joseph Post in 1939. "Almost half of these patients, 45 per cent, were alive at the end of the second year, they now report in the Journal of Clinical Investigations."

### B. Blood Plasma Protein

For many years it has been the desire of investigators and medical men to be able to feed an individual by other than the oral route, for many patients could be benefited and many experiments performed if such a technique were available. One of the difficulties has been the parenteral administration of the protein requirements. An enzymatic digest of meat achieved by Henriques and Anderson was the first success in overcoming this difficulty. Then Holman, Mahoney, and Whipple found that the protein of

<sup>1.</sup> Stafford, Jane, "Possible Cure for Liver Cirrhosis",

p. 10, Science, Dec. 5, 1941

whole plasma can supply the body protein needs. Plasma has been widely used for treatment of shock but its use for nutritional purposes has been restricted by its relatively limited supply; therefore, protein digests should fill this need and supplement all plasma protein treatment. (1)

Elman has found that casein digests intravenously have been used with some success. It has been determined that "an enzymatic (papain) digest of commercial casein given parenterally is as effective in plasma protein production as whole liver by mouth. This digest provides materials needed to correct the hypoproteinemia as well as nitrogen for other body protein requirements."

A great promise in clinical therapy is offered by such a fact.

# C. Miscellaneous Uses

Calcium caseinate is marketed under such names as "Casec", "Larosan", "Roche", and "Protalac". It is merely the casein of cow's milk made partially soluble by combination with calcium. If it is added to gruels and other liquid foods, it is valuable in the treatment of the diarrheal diseases of infancy.

<sup>1.</sup> Madden, S. C., and others, "Casein Digest by Vein Utilized To Form Blood Plasma Protein", Science, April 1941
2. Ibid. p. 331



Likewise, a product known as "Nutrose" or "Nuclio", the sodium salt of casein, is administered as a non-irritant nutrient in the treatment of convalescent, under-nourished, or anemic patients.

The ammonium salt of casein is commercially known as "Eucasein", and it finds use as a nutrient for consumptives and those suffering from stomach or lung ailments.

"Morphine and caffeine preparations are made by triturating the alkaloid with casein in the presence of warm alcohol."

"Saratogen" is sold as a food and tonic, and this product contains about 90% casein. "Sanose", another advertised tonic, contains about 80% casein.

"Silver compounds of casein are used in medicines as substitutes for silver nitrate, which although highly efficient as an antiseptic, yet has a limited use, because of undesirable side reactions, such as irritation, astringency, and corrosion."

An iron nucleo-protein, known as "Proferrin N. N. R.", is used for treatment of blood impoverishment. This proferrin is not affected by the gastric juice, does not

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 380, Reinhold Publishing Corp., New York, N. Y., 1938

<sup>2.</sup> Ibid. p. 381

precipitate albumin, and has no astringent action on the stomach.

Bismuth-Casein compound known as Bismuth Fomic Iodide is used for a healing dressing for wounds, ulcerations, and skin diseases.

Casein Iodine N. N. R. is used in the prevention and treatment of simple or endemic goiter.

A preparation valuable for its astringent action throughout the entire intestinal tract is called "Protan N. N. R.", a combination of tannic acid and an alkali solution of casein.

"The emulsifying and protective power of casein has been used in the development of antiseptic and mildly germicidal silver emulsions much superior to the ointments generally used."

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 381, Reinhold Publishing Corp., New York, N. Y., 1938



### XII. MISCELLANEOUS USES

Besides the major uses already mentioned, casein is an ingredient in many miscellaneous items. Some of these are discussed in the following paragraphs.

### A. <u>Insecticide Sprays</u>

The first work of any importance with casein for such a use was done by the late Professor A. L. Lovett of Oregon Agricultural College, who in 1919 made orchard observations concerning the spreading qualities of various materials. By 1925 the use of casein had increased to an estimated consumption of 300,000 pounds annually, and the economic entomologist of a middle western agricultural college feels that a guess of 1,000,000 pounds annually would not be far from accurate at the present time.

The spray, for example, used to help overcome apple powdery mildew, a serious disease of nursery stock throughout the United States, has casein for one of its materials. The ordinary commercial casein which is used at the rate of 4 ounces to 200 gallons of spray, must be first put in solution, and this is best accomplished by heating it to the boiling point for about 10 or 15 minutes in water to which has been added one-seventh as much sodium hydroxide as casein used. "Calcium Caseinate spreaders may also be obtained commercially and are satisfactory when used

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at the rate of 1 pound to 100 gallons." (1)

Brown-Rot of prunes and cherries is also controlled by a spray in which a casein spreader is effective. This disease is found annually in the prune and cherry orchards of the lower Columbia and Willamette Valleys. If unusually damp weather prevails, a serious epidemic may prevail causing the loss of a large percentage of the crop.

Another use of a caseinate spreader is in the spray used to control the coddling moth which is "the most serious insect enemy of the apples and pears in the Pacific Northwest, taking the region as a whole. Estimated losses from this insect alone run as high as 20% of the total crop of the region in some years. This loss is in spite of the fact that practically all of the growers spray their trees with arsenate of lead from one to six times every season. It is obvious that there is need of improvement both in the timing of the spray and in the method of application."

The use of the spreader has proved very helpful, for it makes it easier to give the fruit a complete coat of poison. Without the spreader, the tendency is to overspray

<sup>1.</sup> Farmers' Bulletin, No. 1120, p. 9, U. S. Department of Agriculture, February 1938

<sup>2.</sup> Farmers' Bulletin, No. 1410, U. S. Department of Agriculture, February 1938

<sup>3.</sup> Farmers' Bulletin, No. 1326, p. 1, U. S. Department of Agriculture, March 1929

and to leave areas between the drops partially or completely unprotected. Also conspicuous white blotches that usually appear on fruit sprayed with the arsenical alone are
eliminated. These blotches interfere with the proper coloring of the fruit and often make it objectionable to prospective purchasers.

Soap and glue may also be used as materials for spreaders, but casein seems to be the most satisfactory, for while some kinds of soap seem to make almost ideal spreaders, they are not put up in convenient forms and are more expensive than casein. While glue is inexpensive, it is inconvenient and some kinds of glue may not work well.

## B. <u>Textile Printing and Finishing Agents</u>

The most extensive use seems to be in the pigment style of calico printing, in the preparation of double cloths as an adhesive, and the finishing and waterproofing of cotton material. The use of casein is as a substitute for albumin in textile printing, but since more work and complications involve from the use of casein, no marked headway has been made in replacing the albumin method.

Another use made of casein in the textile printing industry is its use for protecting and making more durable the surface of the fibres of the color furnisher brushes. These brushes are immersed in a solution of casein and
formaldehyde.

. • It also has been used for giving a high gloss to fabrics, giving them a metallic finish, and for loading silk and cotton.

Professor Louis A. Olney, of the Lowell Textile
School in Lowell, Massachusetts, feels that casein could be
used as dope for tautening aircraft fabric for the wings
and fuselage of airplanes. It would be more fire-resistant
than cellulose acetate, but to date it does not seem to have
been used for such a purpose.

(1)

### C. Soaps and Cosmetics

It is primarily used as a filler in soap and for the purpose of retaining the perfume in cosmetics, such as massage creams and perfume compositions.

## D. Corks

Casein is dissolved in water by borax and sodium phosphate, and glycerin is added. Then cork waste is stirred into this mixture which is then molded into corks or cork discs.

# E. Minor Uses

There are many minor applications of casein of which the following might be mentioned:

1. In liquid cleaners and polishers for white shoes, where it serves as a binder for white pigments.

<sup>1.</sup> Sutermeister and Browne, "Casein and Its Industrial Applications", p. 396, Reinhold Publishing Corp., New York, N. Y. 1938

- 2. For insulating coatings for electrical wirings and machinery.
- 3. For making expensive, natural looking woods by pressing casein solutions into cheaper woods and then hardening them.
  - 4. In compositions used in making matches.
  - 5. In anti-corrosion preparations.
  - 6. In making artificial horsehair.
  - 7. In making liquid court plasters.
  - 8. As an ingredient of paint removers.
- 9. As an antiseptic in paints for hospitals and dairies. Here it must be compounded with formaldehyde.
- make the product less inflammable.
- of latex compositions. as an ingredient of hard rubber and
  - 12. In antiradiation coverings for steam pipes.
  - 13. In mineral oil emulsions.
  - 14. In window shade sizing.

There are still many more uses of casein of a very technical nature, but most of these employ casein in minor quantities or are in the experimental stage.

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XIII. ECONOMIC AND SOCIAL ASPECTS OF THE CASEIN INDUSTRY

A. Benefits to the Farmer

The better utilization of casein and whey is valuable to the farmer, for "the paradox of milk is that the more we use, the more we have. We actually consume all we have, but after we skim the cream, churn the butter, and make the cheese, there are still left over 30,000,000 quarts of valuable skim milk and buttermilk and whey and the dairy industry has a waste product that has a waste product. For when skim milk is run through a casein process more than a billion quarts of whey are left over again." (1) ry of Agriculture, Claude B. Wickard, has asked for repeated increases in the production of milk. For example, in 1942, there was an increase of about 8,200,000,000 pounds above the estimated 1941 production. The Government feels such increases are necessary "for greater use of milk and milk products at home and to supply dairy products for shipment to Great Britain and other nations under the lendlease agreements." (2) Chemurgic outlets provide an answer to the farmer's ever-increasing problem of disposing of his surplus.

The cash farm income has been enlarged by the increase in the production and use of casein. Aralac, for

<sup>1.</sup> Smith, Katherine, "Miracles from Milk" p. 74, Woman's Home Companion, Vol. 69, April 1942
2. Atwood, F. C., Dairy Chemurgy p. 1, 1942

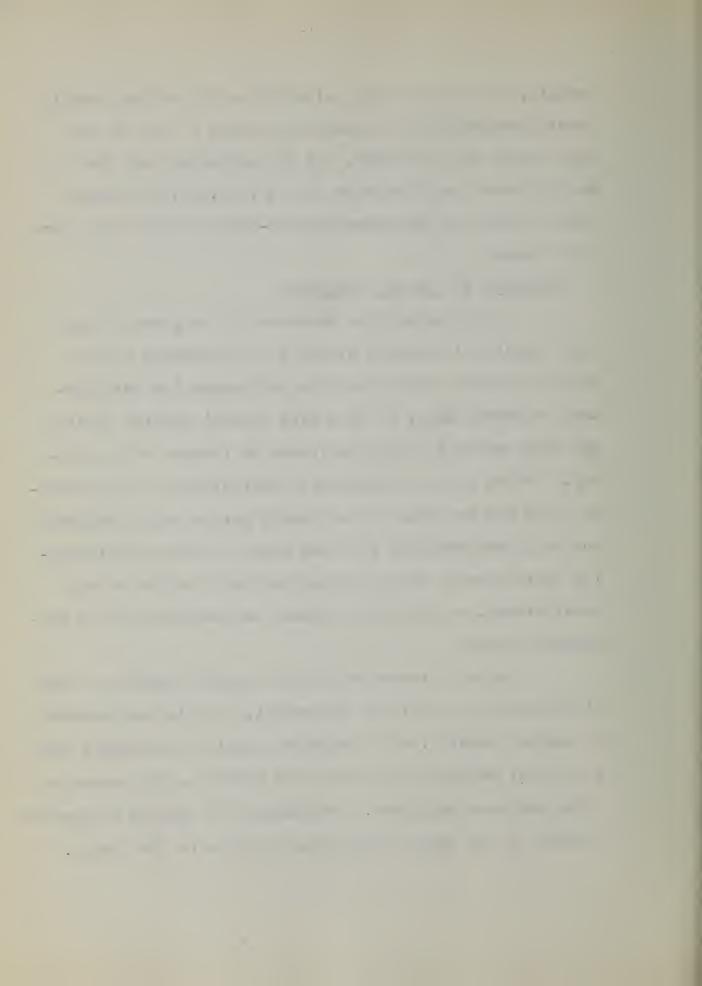


example, is substantially using 25% to 30% of the normal casein production of the country, making a rise in the cash return to the farmer. It was estimated that the dairy farmers received more than \$2,000,000,000 cash income in 1942, or approximately one-fifth of the total farm cash income.

### B. Benefits to the Milk Dealers

milk dealers who separate all or part of their milk supply are affected directly or indirectly by the casein industry. The production of casein (or skim powder, condensed skim, or skim milk cheese) results in larger cash return for milk delivered by farmers to a creamery. In the case of "marginal" manufacturers, no additional price may be added to the amount paid to milk producers, but with the exception of those cases in which manufacturing costs come up to the value received from the casein manufactured, an additional amount can be added to the producers' checks.

Casein production by milk dealers means not only utilization of a waste or by-product, but also an expanded or duplex industry, with increased capital investment, larger plant, much more machinery and perhaps of an expensive type, and more employees. Presumably, it results in greater returns to the dealer and greater returns to the farmer.



In some cases the use of otherwise dumped skim solves the problem of complying with municipal health regulations, as the stench from sewered skim occasionally arouses critical comment from the public.

A comparison of skim value with the cream value of separated milk is interesting. Of 100 pounds of separated milk, roughly 90 pounds are skim and 10 pounds are 40% cream. (Value of cream is reckoned on its butterfat content. Standard cream contains 40% butterfat.) The 90 pounds of skim milk will yield 3% of casein or 2.7 pounds. At 20¢ per pound its value is \$.54. The 10 pounds of 40% cream will contain 4 pounds of butterfat. At 63g per pound its value is \$2.52. Thus, 100 pounds of separated milk bring a cash return of \$3.06. From this comparison it may be observed that our seemingly negligible casein value constitutes one-sixth of the total cash return of separated milk. A further value might be added for 6% of solids recoverable for manufactures or for animal feed. From the farmer's viewpoint, however, it does not follow that one-sixth of the price he receives for his milk is paid for the casein contained therein, for in calculating the farmer's return for cream and skim respectively, one must take the market price of each product and from each deduct the processing costs of the dealer. Cream is mar-



ketable as such, whereas the skim must be precipitated, washed and dried; hence a large proportion of the value is absorbed in costs of production and are not payable to the farmer.

## C. Benefits to the Public

The public also derive several benefits from the growth of the casein industry. In the first place, it enables them to procure a greater variety of articles, many of them at a lower cost than would otherwise be possible. For example, by the use of Aralac, many of the qualities of higher priced fabrics can be secured at a price not far in excess of cotton and rayon. The plastics industry has come to the aid of the home, office, and factory by offering substitutes for much of the metal formerly used, and in many cases has produced a more adaptable product.

Since there are probably twenty million human beings whose health and happiness are tied to farms, and since dairying, including the manufacturing, distribution, and sale of products constitutes the world's largest industry the health and prosperity of the entire country are affected by any trend in the casein industry. "The problem of a country's milk supply affects government policy, trade, and even the strategy of war" for "today milk can feed factories as well as people."

<sup>1.</sup> Smith, Katherine, "Miracles from Milk" p. 70, Woman's Home Companion, Vol. 69, April 1942



Casein appears destined to play an increasingly important role in the United States war effort, for "the United States War Production Board states that, of all the chemical materials it has studied, casein offers the best possibilities as a practical substitute material in many kinds of industry. Thousands of manufacturers can use the product, it is stated, since it cuts across industrial lines in almost every field and can aid materially in relieving shortages of chemical substances that are required for the manufacture of war implements."

## D. Future of the Industry

As for the future of the casein industry, it is reasonable to expect that the present trend of increased use of casein will continue since there is constant dairy research being carried on to discover new uses and new markets for milk by-products. National Dairy Products Corporation, the largest dairy corporation in the world, has a division known as Atlantic Research Associates, Inc., which devotes its efforts to dairy chemurgy.

One of the biggest problems yet unsolved is the transportation of skim milk. A possible solution might be a method by which casein could be produced right on the farm, but so far all research in this direction has proved unproductive.

<sup>1.</sup> Foreign Commerce Weekly, "Dive Bombers from Skimmed Milk", p. 9, August 1942



eration. At the end of 1941 the Ford Motor Car Co. announced that it was producing 1000 pounds per day of a soybean fibre that closely resembles wool at considerably less than half the cost of sheep's wool. While it is expected that the early production of it will be used for auto upholstery, Henry Ford already is wearing a soybean fibre suit, so it might soon offer keen competition to Aralac. In other fields also has casein found a rival in this soybean protein, glue being one example.

How many of the casein articles now being used as substitutes for "priority" articles will continue in use after the War remains a question. Dr. Atwood, however, has objected to Aralac being used as a temporary substitute for wool. In a speech presented on February 27, 1942, to the American Association of Textile Chemists and Colorists, he said:

"We are most concerned that present uses of Aralac are suitable and in line with its unique characteristics. Certainly, none of us would gain much if Aralac is used as a wool substitute during the present emergency. We will help take care of any military requirements. We will cooperate in every way to find uses for which Aralac has a permanent and acceptable field. But we would decry any use wherein Aralac would be but a temporary substitute for wool.

"We wish for Aralac that it find its way into the textile industry on its own merits and when and if conditions return to normal, Aralac will have become a new staple fiber low in cost but high in intrinsic value."



If one can believe the following picture of how casein will soon affect the daily routine of men and women, certainly the future of the casein industry is a bright one.

"Soon you will be crawling out from under blankets made of milk, spread on a bed held together with milk. A rug of milk will protect your bare feet from the cold, milk-coated floor. You will turn on a faucet handle of milk to take your morning shower, after which you will shave with a milk-handled razor, comb your hair with a comb of milk, brush it with a milk-backed brush, and inspect the result in a milk-backed mirror. Then you will don a suit of warm milk wool, held in place by buttons of milk, and will be ready for a breakfast of cream-drenched cereal served in a bowl made of milk and eaten with a milk spoon. The transparent film of milk protecting the breakfast food from the elements may crackle as it is removed. When you climb into your automobile, you will turn on the milk ignition knob, and your hand will grip the milk gearshift lever. Upon arriving at the office, you will get to work with your milk-barreled fountain pen and write a check on a sheet made of milk-surfaced paper. And if you do not feel like working, you may thumb through the glossy, milk-coated pages of a popular magazine." (1)

# E. Conclusions

It is significant that the casein industry adds more than ten million dollars annually to the return from milk products, without the addition of any raw material. From a slow beginning, accentuated by the failure to produce a uniformly high quality product, the industry has grown to such an extent that today it forms a valuable outlet for

<sup>1.</sup> The Christian Science Monitor, Sept. 8, 1938 (Excerpt from a report describing the Milwaukee Meeting of The American Chemical Society)



skim milk. From its infancy in 1900, casein production increased by 1940 to 50,000,000 pounds obtained from 1,500,000,000 pounds of skim milk. Implications of its growth and further possibilities may be discerned from the fact that in 1920 only three to four per cent of the available skim milk was used in manufactured products as compared with twenty per cent so used in 1940.

Much of its growth can be attributed to research efforts to fit the favorable qualities of casein into products in which it is superior to its competitors. Long had this complex protein casein been recognized as containing vast possibilities, and today it appears that some dreams are becoming commercial realities. An important factor in the increased use of casein is the fact that manufacturers and users of it have become better acquainted with its unique characteristics and idiosyncrasies. Casein paints have met with increased favor in recent years and today are found adaptable in blackout and camouflage work. In glues, casein's superior qualities were discovered during the World War period and since that time it has contributed to the success of plywood and veneer industries. In the field of plastics, although mass production is yet limited, beautiful articles of fine quality are being made. Scarcity of vital metals at the present time has flooded the demand

for synthetics and casein plastics are meeting requirements for this need. In foods and medicines, volume of outlet (except casein contained in cheeses) is small to date. However, it fulfills requirements for particular needs not met as well by potential substitute products. Casein fibre is perhaps the newest product to find its way onto the market and already it has made a spectacular success in American textiles. The use of casein in paper coating, although decreased today, has been the major outlet for this milk by-product. Its steady use in this industry will probably continue.

The casein industry has passed through the stage of utilization of a waste-product into a by-product industry in its own rights. Rating the two milk derivatives, cream and skim, intrinsically, the skim ought to be valued at more than the cream. Hence, it is not absurd to perceive a possibility of a reversal in values.

In considering the advancement of casein uses, one might ask, "What is next?" Might it be that from separated milk, the cream will be used for butter, the skim used for casein, and the casein whey, whose 6% solids consist mainly of milk sugar, be converted into alcohol, and the alcohol used for synthetic rubber? We do know that alcohol is obtainable from milk whey, but for further information we shall have to look to the future.



#### BIBLIOGRAPHY

#### BOOKS:

- Berry, P. G., "Stuff", Appleton Publishing Co., New York, 1930
- Fisk, W. W., "Commercial Casein", Olsen Publishing Co., Milwaukee, Wisconsin, 1923
- Hadert, Hans (Trans. by Dr. Henry Goldsmith) "Casein and Its Uses", Chemical Publishing Co. of New York, New York, 1938
- Scherer, Robert, "Casein", Scott, Greenwood & Son, London, 1921
- Sutermeister and Browne, "Casein and Its Industrial Applications", Reinhold Publishing Corp., New York, New York, 1938
- Tague, Edgar Lemuel, "Casein, Its Preparation, Chemistry, and Technical Utilization", D. Van Nostrand Co., New York, 1928

### ARTICLES AND OTHER SOURCES:

- Agricultural Leaders' Digest, "Why Casein Paint Steadily Makes Friends", Sept. 1938
- Anderson, A. B., "Casein Production: Abstract", Food Industries, Vol. 14, August 1942
- Aralac, Inc., "Aralac", New York, N. Y.
- Aralac, Inc., Pamphlet "The Cow, the Milkmaid, and the Chemist", New York, N. Y.
- Atwood, F. C., "Aralac", American Dyestuff Reporter, Vol. 31, March 30, 1942
- Atwood, F. C., "Aralac, a Newcomer in the Galaxy of Textile Fibres", Chemical Industries, Vol. 49, Dec. 1941
- Atwood, F. C., "Character of Aralac Casein Textile Fiber", Women's Wear Daily, January 20, 1942

- Atwood, F. C., "Chemurgic Products from Milk", speech presented at the First Annual Southern Chemurgic Conference, Nashville, Tennessee, June 19, 1941
- Atwood, F. C., "Dairy Chemurgy", speech presented at the Eighth Annual Chemurgic Conference, Chicago, Illinois, March 25, 1942
- Atwood, F. C., "Modern Casein Paints", Plastic Products, Vol. 10, March 1934
- Atwood, F. C., "Natural Protein Base Spun Fibers", American Dyestuff Reporter, March 17, 1941
- Atwood, F. C., "Rabbits from Hats", Seventh Annual National Farm Chemurgic Conference, Chicago, Illinois, March 26, 1941
- Atwood, F. C., "The Dairy Industry and Chemurgy", speech presented at Second Mid-American Chemurgic Conference, Cleveland, Ohio, Sept. 16 and 17, 1940
- Automotive Industries, "Lanital; Synthetic Flax from Milk", Vol. 76, January 30, 1937
- Birrell, T. L., "Casein Plastics", Modern Plastics, Vol. 6, October 1938
- Brother, O. H., "Casein Plastics", Industrial and Engineering Chemistry, Vol. 32, January 1940
- Brown, H. H., and Webb, B. H., "Canned Whey Pudding--A New Product", Food Industries, Vol. 13, No. 11, Nov. 1941
- Business Week, "Casein at the Bat: Product of Many Uses", September 12, 1942
- Business Week, "Fibres from Milk: Aralac", November 22, 1941
- Business Week, "Hats Made With Milk", October 12, 1941
- Casein Company of America, "Protovac", Bainbridge, New York
- Christian Science Monitor, "Fibers of Milk Used to Make Better Clothes", November 10, 1941
- Christian Science Monitor, September 8, 1938

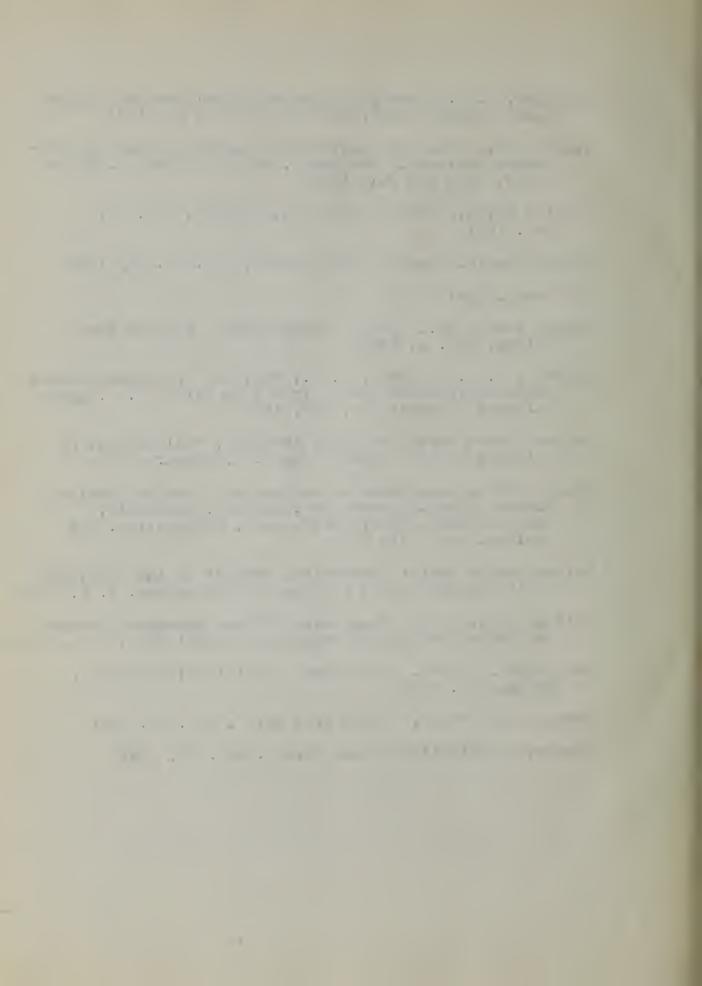
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- Davis, Watson, "Plastics in Defense", Science News Letter, November 15, 1941
- Diamond, C., and Wormell, R. L., Ph. D., "The Manufacture and Properties of Casein Fibre", Textile Recorder, June 6. 1939
- Ducrot, J. A., "Wool from Milk", Magazine Digest, Feb. 1936
- Engineering, "Artificial Wool Manufacturing in Italy", Vol. 144, December 17, 1937
- Farmers' Bulletin, No. 425, "Experiment Station Work, LX", U. S. Dept. of Agriculture, Sept. 1910
- Farmers' Bulletin, No. 1410, "Control of Brown-Rot of Prunes and Cherries in the Pacific Northwest", U. S. Dept. of Agriculture, March 1924
- Farmers' Bulletin, No. 1326, "Control of the Coddling Moth in the Pacific Northwest", U. S. Dept. of Agriculture, March 1929
- Farmers' Bulletin, No. 1120, "Control of Apple Powdery Mildew", U. S. Dept. of Agriculture, Feb. 1938
- Food Industries, "By-Products of Milk", October and November 1937
- Food Industries, "Fibres from Milk: Aralac", Dec. 1941
- Food Industries, "Wine Made from Milk", Jan. 1941
- Foreign Commerce Weekly, "Casein Plastics Industry in 1941", Vol. 7, April 11, 1942
- Foreign Commerce Weekly, "Dive Bombers from Skimmed Milk", Vol. 8, August 1942
- Greenleaf, F. M., "As Beta Lactose Becomes a Food", Food Industries, August 1933
- Hall, A. J., "Improving Casein Fibres", Textile Colorist, Vol. 63, December 1942
- Heim, G., "Casein Fibre", Textile Recorder, June 6, 1939

- Hoard's Dairyman, "Milk Wool for Hats", Dec. 15, 1940
- India Rubber, "Latex: Casein Adhesives", Vol. 101, March 1940
- LaRose, Paul, "Casein Wool", Canadian Textile Journal, April 17, 1936
- Little, A. D., "Paint from Milk", Scientific American, September 1934
- Lowry, J. V., and others, "Treatment of Dietary Liver Cirrhosis in Rats with Choline and Casein", Bibliography Public Health Reports, Vol. 56, Nov. 14, 1941
- Madden, S. C. and others, "Casein Digest by Vein Utilized to Form Blood Plasma Protein", Science (new series), Vol. 93, April 1941
- Manufacturing Record, "Textile Fiber Derived from Milk", Vol. 107, April 1938
- Miller, Mack, and Chapman, "The Identification of Nylon and of Lanital Textile Fibers", Journal of Home Economics, April 1941
- Milwaukee Journal, "Hats from Skimmed Milk", Dec. 11, 1941
- Modern Plastics, "Textiles from Casein Protein Fiber", Vol. 19. Dec. 1941
- Modern Plastics Catalog 1942, Buskin Publishing Corp., New York, New York
- National Butter and Cheese Journal, Feb. 1939
- National Dairy Products Corporation, "Casein, Milk Protein Has Diversified Uses", New York, New York
- National Farm Chemurgic Council, Feb. 10, 1941
- National Farm Chemurgic Council, Aug. 25, 1941
- National Farm Chemurgic Council, Nov. 19, 1941
- Nature, "Preparation of Thyroxine from Casein", Vol. 144, July 29, 1931

- New York Times, "Cows Make Wool in Ohio Village", Aug. 26, 1940
- New York Times, "New Casein Fiber Due for Wide Use", Nov. 9, 1941
- Paper Trade Journal, "Casein for Paper Coating", Vol. 96, January 26, 1933
- Paper Trade Journal, "Casein in New Trade Agreement with Uruguay", Vol. 115, July 30, 1942
- Popular Mechanics, "A New Age of Glue", September 1937
- Rayon, "New Casein Fiber Aralac Now an Assured Success in Textile Manufacturing", Vol. 22, Nov. 1941
- Rural New Yorker, "By-Products of the Dairy Industry", May 8, 1937
- Rural New Yorker, Nov. 6, 1937
- Science, "Milk as a Raw Material for Industry", Vol. 89, Sup. 12, April 7, 1931
- Science News Letter, "New Process Makes Fabrics from Cow's Milk", Nov. 15, 1941
- Science News Letter, "Whey to Make Candy", Feb. 1, 1941
- Scientific American, "Rubber-Like Substance from Dairy By-Products", Vol. 160, June 1939
- Smith, Katherine, "Miracles from Milk", Women's Home Companion, Vol. 69, April 1942
- Smithsonian Report for 1941, "The New Synthetic Textile Fibers", Smithsonian Institute, Washington, D. C.
- Stafford, Jane, "Possible Cure for Liver Cirrhosis", Science, Vol. 94, Sup. 10, Dec. 5, 1941
- State of California Department, "Statistical Report of California Milk Products", 1941
- Steel, "Water Thinned Casein Paint Shown to Have Many Desirable Features", Vol. 100, Jan. 25, 1937

- Stringer, W. E., "Profits from By-Product Recovery Depend upon Products Made", Food Industries, May 1931
- Textile Colorist, "New Synthetic Fiber from Casein by Procedure Devised by Stephen P. Gould and Earl O. Whittier", June and July 1938
- Textile World, "Fibres from Milk: Aralac", Vol. 91, Nov. 1941
- Textile World, "Lanital Production", Vol. 88, May 1938
- The Index, April 1932
- Thone, Frank, Dr., "Whey to Make Candy", Science News Letter, Feb. 1, 1941
- Thimble, C. S. and Bell, R. W., "Methods for Manufacturing Acid-Precipitated Casein from Skim Milk", U. S. Agricultural Circular. No. 279, 1933
- United States Bureau of Dairy Industry, Publications of Articles by Lee T. Smith and H. V. Claborn
- United States Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisconsin, "Casein Glues: Their Manufacture, Preparation, and Application", July 1939
- United States Tariff Commission, "Report to the President of the United States on Casein", Washington, D. C., 1926
- United States Tariff Commission, "Trade Agreement Between the United States and Argentina", Washington, D. C., 1942
- Von Bergen, Werner, and Krauss, "Textile Fiber Atlas", Rayon, Nov. 1940
- Weekly News Review, "Cloth from Milk", Nov. 28, 1941
- Wisconsin Agriculturist and Farmer, Nov. 29, 1941





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